OPTIMUM SELECTION OF VES SYSTEMS AS EOR FLUID FOR WAFRA RATAWI FIELD

BY

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Dedication

I dedicate this effort to my parents and siblings; the reason of my success in every step of my life and for their love, patience and support

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All praise to the Almighty for his countless blessings bestowed upon me and giving me the strength to complete this work. Without His help, nothing is possible. No words of thanks are enough to express my gratitude towards Him.

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LIST OF ABBREVIATIONS

EOR	:	Enhanced Oil Recovery
cEOR	:	Chemical EOR
IFT	:	Interfacial Tension
CA	:	Chelating Agent
VES	:	Viscoelastic Surfactant
VES-CA	:	Viscoelastic Surfactant with Chelating agent
TGA	:	Thermogravimetric analysis
API	:	American Petroleum Institute
DTPA	:	Diethylene Triamine Penta Acetic acid
FTIR	:	Fourier Transform Infrared
NMR	:	Nuclear Magnetic Resonance
ICP	:	Inductively Coupled Plasma

ABSTRACT (ENGLISH)

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Interfacial Tension (IFT) and mobility control are two main mechanisms that are the deciding factors for the success of any EOR process. Carbonate reservoirs rocks are usually characterized by the low permeability matrix with high fractures, and have always been remain the biggest challenge for the chemical EOR. In general, cEOR methods cannot be applied to reservoirs that are deep and have high temperature and salinity because of the degradation of chemicals. Viscoelastic Surfactant has proved to be a good fluid for cEOR.

Viscoelastic surfactants are known to be the best for cEOR applications because of its dual nature of reducing the oil/water interfacial tension (IFT) and improving the sweep efficiency. In this work, a systematic study is carried out to test the applicability of a novel viscoelastic surfactant for recovering heavy oil from the carbonate reservoir. Our aim is to identify the best VES based formulation suitable for cEOR application in Ratawi Oolite reservoir in the Wafra-Ratawi Field. Our objective in the work is to explore and optimize VES, or VES with chelating agent (VES/CA) systems as novel EOR methods in carbonate reservoirs. The introduction of VES/CA is suggested to balance the effect of divalent salts on VES. Chelating agents are known for their affinity to salts. Their use would likely reduce the impact of the very high levels of divalent salts on VES (salt balance). The Ratawi field has exceptionally high levels of divalent cations. Ultra-low interfacial tension

of VES and VES-CA systems is determined using spinning drop tensiometer. Thermal stability of VES systems in sea water and compatibility of VES systems by combining VES with chelating agents is evaluated. Moreover, adsorption effect of VES on carbonate samples is also studied and experimental results are plotted with Langmuir and BET isotherm models. In addition, zeta potential measurements for both VES and VES/CA systems are evaluated for supporting the results of adsorption. Dynamic adsorption is determined by performing core flood experiments. Two experiments of core flooding are performed i) with sea water and VES flooding, ii) with sea water and VES/CA flooding. Effluent analysis is carried out for the solutions collected at the outlet of core flood system. The results of both experiments are evaluated.

Results of this study indicate viscoelastic surfactant is a suitable option for cEOR to recover additional oil from the reservoir. Ultralow IFT's, thermal stability and adsorption obtained with viscoelastic surfactant showed that they are excellent additives that can be used in cEOR for HTHS conditions. They are also very useful when we have heavy oil reservoirs and where IFT reduction is required to mobilize the oil and improve the sweep efficiency of the reservoir.

ABSTRACT (ARABIC)

ملخص الرسالة

الاسم الكامل: انيق ناصر جنجوعه

عنوان الرسالة: الأختيار الأمثل لأنظمة معاج اللزوجة السطحية كمادة لأستخراج النفط المعزز في حقل وفرة راتاوي

التخصص: هندسة البترول

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التوتر السطحي والتحكم في التنقل هما الآليتان الرئيسيتان لنجاح أي عملية من عمليات استخلاص النفط المعزز. وعادة ما تتميز مكامن النفط المكونة من صخور الكربونات بنفاذية منخفضة مع وجود تشققات بنسبة عالية، وكانت دائما تشكل أكبر تحد لاستخلاص النفط المعزز كيميائيا. وبوجه عام، لا يمكن تطبيق طرق الاستخلاص الكيميائي المعزز للنفط على المكامن العميقة ذات درجة الحرارة العالية والملوحة بسبب تفكك المواد الكيميائية. وقد ثبت أن معالج اللزوجة السطحية هو سائل جيد للاستخلاص الكيميائي المعزز للنفط.

ومن المعروف أن معالج اللزوجة السطحية هو الأفضل لتطبيقات استخراج النفط المعزز الكيميائي بسبب طبيعته المزدوجة للحد من التوتر بين النفط و الماء وتحسين كفاءة الاجتياح. في هذا العمل، يتم إجراء دراسة منهجية لاختبار قابلية تطبيق معالج لزوجة سطحية جديد لاستعادة النفط الثقيل من مكامن الصخور الكربونية. هدفنا هو تحديد أفضل تركيبة لمعالج لزوجة سطحية على أسس مناسبة للاستخدام الكيميائي لاستخراج النفط المعزز في خزان راتاوي أوليت في حقل الوفرة راتاوي. هدفنا في العمل هو استكشاف وتحسين معالج اللزوجة السطحية ، أو معالج اللزوجة السطحية مع أنظمة عامل الانتزاع كطرق جديدة لتعزيز استعادة النفط في مكامن الصخور الكربونية. اقترح إدخال معالج اللزوجة السطحية مع عامل الانتزاع لتحقيق التوازن بين تأثير الأملاح ثنائية التكافؤ على معالج اللزوجة السطحية. وتعرف عوامل الانتزاع بتشابهها مع الأملاح. ومن المرجح أن يقلل استخدامها من تأثير مستويات الأملاح ثنائية التكافؤ العالية على معالج اللزوجة السطحية (توازن الملح). حقل راتاوي لديه مستويات عالية بشكل استثنائي من الكاتيونات ثنائي التكافؤ. يتم تحديد التوتر السطحي المنخفض جدا لمعالج اللزوجة السطحية و معالج اللزوجة السطحية مع عامل الانتزاع باستخدام مقياس التوتر السطحي المغزلي. يتم تقييم الثبات الحراري للأنظمة معالج اللزوجة السطحية في مياه البحر ومدى توافق أنظمة معالج اللزوجة السطحية عن طريق الجمع بين معالج اللزوجة السطحية مع عوامل الانتزاع. وعلاوة

على ذلك، يتم دراسة تأثير الامتزاز من معالج اللزوجة السطحية على عينات الصخور الكربونية و تمت مقارنة النتائج التجريبية مع نماذج لانغمویر و ب.ا.ت . وبالإضافة إلى ذلك، يتم تقييم القياسات المحتملة زيتا لكل من معالج اللزوجة السطحية و معالج اللزوجة السطحية مع عامل الانتزاع لدعم نتائج الامتزاز. يتم تحديد الامتزاز الديناميكي عن طريق إجراء التجارب الضخ الأساسية. يتم إجراء تجربتين من تجارب الضخ الأساسية 1) ضخ مياه البحر و معالج اللزوجة السطحية ، 2)ضخ مياه البحر و معالج اللزوجة السطحية مع عامل الانتزاع. يتم إجراء تحليل النفايات السائلة للمحاليل التي تم جمعها في منفذ نظام الضخ الأساسي. يتم تقييم نتائج كل من التجارب.

وتشير نتائج هذه الدراسة إلى أن معالج اللزوجة السطحية هو خيار مناسب لاستعادة النفط المعزز كيميائيا لاستعادة النفط الإضافي من المكمن. وأظهرت نتلئج التوتر السطحي المنخفض والاستقرار الحراري والامتزاز التي تم الحصول عليها مع ا معالج اللزوجة السطحية أنها إضافات ممتازة يمكن استخدامها في استخلاص النفط المعزز كيميائيا عند درجات الحرارة و الملوحة المرتفعة. كما أنها مفيدة جدا عندما يكون لدينا مكمن نفط كثيف وحيث يتطلب الحد من التوتر السطحي من أجل انتاج النفط وتحسين كفاءة الاجتياح في المكمن.

CHAPTER 1

INTRODUCTION

1.1 Enhanced Oil Recovery (EOR)

Crude oil reservoirs are found in almost every region. Traditional means of recovery such as natural depletion and pressure maintenance leave a great amount of oil in the reservoir. So there remains the need to recover that residual oil from the reservoir. For that another recovery method known as enhanced oil recovery (EOR) is applied to recover the remaining oil in the reservoir. In the recent years EOR has gained much importance because of its potential application in heavy crude oil reservoirs. EOR is a tertiary recovery process in which a variety of techniques are applied for supplementary recovery of crude oil from the reservoir. For this an external fluid or heat is injected into the reservoir that provides sufficient energy in addition to the natural energy to mobilize oil towards the producing well. The injected fluids usually come in contact with the rock/oil in the reservoir to create conditions that are favorable for the residual oil recovery. These interactions might, for example, result in oil viscosity reduction, lower interfacial tension (IFT), oil swelling, wettability alteration, or favorable phase behavior. The interactions are attributable to physical and chemical mechanisms and the injection or production of thermal energy [1].

The main goal of EOR process is to alter the mobility and to increase the capillary number in the reservoir. As long as water flooding technique is economically feasible it is preferred.

Over long-time periods remaining oil is left in pores in the reservoir after the primary and secondary recovery operations, where the oil is trapped, mainly due to viscous forces and capillary forces. EOR techniques provide sufficient energy that ultimately increases the lifetime of reservoirs. EOR improves the sweep efficiency of the reservoir and reduces the remaining oil saturation. Unfortunately, the application of EOR is associated with higher risks and does not bring only advantages and increases the requirement for additional facilities and investments. Selection of suitable EOR process for a reservoir depends on many factors like oil and rock properties, its economic feasibility, technology and availability of raw materials. Improving the recovery factor can be achieved by deploying advanced IOR technologies using best-in-class reservoir management practices, and EOR technologies [2].

1.2 Oil Recovery Methods

Oil extraction techniques have been divided into three main stages i.e. primary, secondary and tertiary recovery. Usually the former two techniques bring only quarter to half of oil reserves present in the reservoir whereas the latter technique (tertiary recovery) has been developed to recover residual oil more efficiently than primary and secondary recovery techniques.

1.2.1 Primary Recovery

Primary recovery deals with the recovery of oil by the natural depletion of reservoir. Oil is forced to the surface by the subsurface pressure. Presence of gaseous fuels, natural gas or water in the reservoir also supports the pressure needed for the oil to reach the surface. With time, the reservoir pressure falls and hence the differential pressure also decreases which may necessitate the use of pressure maintenance or injection of water or gas to

increase production. When the reservoir pressure becomes too low, or the ratio of gas or water to oil in the output stream is too high then it means that the limit for the primary recovery has reached.

1.2.2 Secondary Recovery

Secondary recovery technique is applied in the reservoir when there is only small fraction of oil recovered by the reservoir's natural drive. Oil recovery is made by the injection of water or gas, generally for pressure maintenance and macroscopic sweep efficiency. This method is applied until we obtain effective production from the reservoir and which is economically feasible. Over the time of reservoir production, the water production may increase and it can cause decrease in the oil production. There comes the time when there is very less oil production and we get more water in the output stream. This is the limit for the secondary recovery operation and all the oil that can be recovered from reservoir with injection of water or gas has been recovered economically. Remaining oil is left over in the reservoir that brings us the need for the tertiary recovery. Typically, additional recovery of about 10-20% oil is obtained than primary recovery.

1.2.3 Tertiary Recovery

The techniques applied after the secondary recovery to recover the residual oil are generally considered as tertiary recovery. These techniques are used to displace the left-over oil in the reservoir after the secondary recovery has become uneconomical. Residual oil is recovered by the introduction of some external source such as chemicals, steam, miscible gases, or by the injection of heat energy in the reservoir. Tertiary recovery methods generally improve the sweep efficiency of the reservoir or decrease the remaining oil saturation in the reservoir. Through the process of EOR the zones that are left over before

by the secondary recovery are swept and also it recovers the trapped oil in the pores because of the capillary forces. This all depends on the implementation and selection of the technique in EOR. These recovery methods usually change the mobility ratio and reservoir fluid properties and create the pressure difference between the reservoir and production wells to recover the remaining oil saturation in the reservoir. Although these methods are not capable of recovering the whole remaining oil saturation in the reservoir but still they recover substantial amount of oil from the reservoir.

1.3 Categorization of EOR Processes

The main purpose of all EOR methods is to recover the residual oil that is left over after the primary and the secondary recovery. EOR focuses on increasing the volumetric sweep efficiency and on enhancing the displacement efficiency, unlike usual waterflood mechanism. One mechanism focuses on increasing the sweep efficiency by reducing the mobility ratio between the both displacing and displaced fluids. Since the mobility of the injected fluid is reduced, the effect of viscous fingering is lowered.

The other mechanism increases the capillary number by reducing the amount of oil trapped due to the capillary forces. By reducing interfacial tension between the fluids, the effect of microscopic trapping is lowered, giving a low remaining oil saturation and higher ultimate recovery. So, the ultimate recovery factor depends on the microscopic displacement efficiency and on macroscopic displacement efficiency [3].

In general, EOR processes can be categorized into four major categories:

1.3.1 Chemical EOR

This process involves injection of different chemicals in the reservoir to recover the remaining oil. Chemical EOR methods can give both microscopic displacement efficiency and macroscopic sweep efficiency [4]. The chemical processes refer to those processes in which additional non-natural components are added to the fluids to stimulate the mobility between both the displacing and displaced fluid. Chemical EOR can be divided into different processes like surfactant flooding; that changes the wettability of the formation rock and reduces the interfacial tension, polymer flooding; which is used to improve the sweep efficiency of the invading fluid by changing the mobility ratio between the invading fluids and the displaced fluid, caustic flooding; caustic reacts chemically with the fatty acids present in the petroleum derivatives and form in-situ sodium salts of fatty acids, alkaline flooding; in which an alkaline chemical, such as hydroxide, carbonate or orthosilicate of sodium, is injected in a slug form. The alkaline chemical reacts with the acid components of the crude oil and produces the surfactant in situ that reduces the IFT, and alkali surfactant-polymer (ASP) flooding; in which combination of alkaline, surfactant and polymer are injected in the same slug [5]. In the recent years, viscoelastic surfactant (VES) flooding has gained much importance because of its dual capability to mobilize the trapped oil. Both the mobility ratio and capillary number are affected using VES as an EOR fluid. It provides better displacement of the trapped fluid and recovers the remaining oil by reducing the IFT. So, it has the qualities of both surfactant as well as polymer.

1.3.2 Gas EOR

In Gas EOR different gases like natural gas, nitrogen and carbon dioxide (CO_2) are injected to recover the remaining oil in the reservoir. Oil is made to displace towards the production well by the reduction of viscosity and improving its flow rate.

In carbonate reservoirs that are heterogeneous, sole injection of gases may cause channeling or overrun problems due to the low density and less viscosity of gases. To avoid these problems a mobility control agent should be used. Viscoelastic surfactant has the advantage that it has the dual capability of providing both the better sweep efficiency and lowering the IFT [6].

In Gas EOR there are two types of flooding i.e. miscible and immiscible flooding. In miscible flooding, gas is injected into the reservoir that reacts with oil reduces its viscosity and forms a miscible bank. This bank acts like a slug and water flooding is done after that to improve the sweep efficiency. The miscible fluid is generally less viscous than the oil and tends to "finger" through the oil. In immiscible flooding, the main mechanisms involved are viscosity reduction, oil swelling, extraction of lighter hydrocarbons, and mobility. In general, immiscible gas EOR is much less efficient than miscible gas EOR in recovering the oil remaining in the reservoir.

1.3.3 Thermal EOR

Thermal EOR methods generally improve both the oil displacement efficiency and the volumetric efficiency by the introduction of heat into the reservoir that raises the temperature and reduces the viscosity of oil. Thermal methods are best suited for heavy oil

reservoirs. The production mainly comes from regions possessing huge quantity of heavy oil reserves such as Canada, Venezuela and China.

In this process heat is injected in the reservoir that lowers the viscosity of oil and extracts smaller fractions from oil for more displacement. Thermal processes use heat in well bores to increase the production rates for heavy crude oils. The increase in heat reduces the surface tension and increases the permeability of the oil and improves the reservoir seepage conditions. Thermal EOR methods are of different types; mainly hot water flooding, steam flooding, in situ combustion and electrical heating are used. From them steam flooding is more commonly used process and is more efficient than other processes. Cyclic steam stimulation (CSS) has been in use since 1960's in California [5].

In hot water flooding, viscosity of oil is reduced by the injection of hot water that displaces the oil and improves the sweep efficiency and reduces the remaining oil in place. When hot water is injected continuously it may swell the clay matrix and increase the porosity and permeability. Also, there are heat losses in the well bore and there is difference in the temperature at wellhead and formations.

Steam flood process reduces the viscosity of oil by the injection of steam in the reservoir. As the steam condenses, the steam distilled components also condense and form a solvent front that will assist in displacing heavy oil as a mixture of solvent and oil towards the production well. Depending on the oil viscosity, certain thermal EOR methods have to be implemented right from the initial stage. Thickness of the reservoirs is the major factor restricting the steam flooding applications. However, thin reservoirs are accounting for huge heavy oil reserves [7].

The heated oil may also vaporize and then condense forming improved oil. This approach however, requires substantial investment in special equipment. Both thermal recovery methods also severely damage the underground well structure, as well as pose safety risks in the larger production process. High quality steam is injected in the production well. After pumping down the pressurized steam for weeks and sometimes months, the process is halted, usually for several weeks, which allows the heavy oil to separate from the reservoir sand, and then it is artificially lifted. Normally steam travels on the top of the sand and gravity helps the oil to resaturate the steam zone, from where it is displaced towards the wells.

In-Situ combustion gained much importance during 1950's when many publications were made in this area and until the 1960's most of the projects of thermal oil recovery related to this process. In-Situ combustion applies on the reservoirs that contain low gravity oil, which is heated with the help of air injection. The oil is then driven out of the reservoir with the help of steam, hot water or gas drive, as it becomes less viscous. Either dry or moist air can be injected. The fire propagates from the air injection well to the producing well, moving oil and the combustion gases to the front.

Electrical heaters have been thought of as solution for many years. However, the technical capabilities of low voltage (fewer than 600 V) have limited the use because of parasitic energy loss in the overburden and short lengths of heaters in horizontal wells. These two detractors have made low-voltage heaters uneconomic for commercial applications, while numerous short-length pilots (up to 250 ft) have proven this technique of viscosity reduction to be technically feasible but not economic.

1.3.4 Microbial EOR

Microbial EOR (MEOR) flooding involves the injection of microorganisms that react with reservoir fluids to assist in the production of residual oil. Microbes can be used to improve oil recovery. MEOR has always been an attractive EOR method due to its low cost and potential to improve both microscopic and macroscopic displacement efficiencies. However, the uncertainties, sensitivities and time constraints of biological agents have always limited their success and application potential. Nevertheless, MEOR has introduced the use of organic substitutes for chemical EOR methods.

There are two general types of MEOR processes: those in which microorganisms react with reservoir fluids to generate surfactants and those in which microorganisms react with reservoir fluids to generate polymers. MEOR relies on microbes to ferment hydrocarbons and produce by-products such as bio surfactants and carbon dioxide that help to displace oil in a similar way than in conventional EOR processes. MEOR refers to the use of microorganisms to retrieve additional oil from existing wells, thereby enhancing the petroleum production of an oil reservoir.

1.4 Mechanisms of EOR Process

Improving the microscopic and macroscopic displacement efficiency increases the overall oil displacement efficiency, which is the ultimate goal of EOR processes.

Microscopic displacement efficiency displaces oil at the micro scale and measures the effectiveness of displacing fluid in mobilizing the oil at those places in the rock where the displacing fluid contacts the oil. It is affected by;

- Wettability

- Interfacial tensions (IFT)
- Capillary Pressure

Macroscopic displacement efficiency gives us the efficiency of the displacing fluid when it contacts with the reservoir in a volumetric sense. Macroscopic displacement efficiency also known as conformance indicates how effectively the displacing fluid moves the displaced oil toward production wells and how useful the displacing fluid is in sweeping out the volume both areally and vertically of a reservoir. It is affected by;

- Fluid density difference
- Anisotropy and rock heterogeneity
- The mobility ratio

1.4.1 Mobility Ratio

Mobility ratio (M) is given as the fraction of mobility of the displacing fluid to the mobility of displaced fluid [8].

$$M = \frac{Mobility\ of\ displacing\ phase}{Mobility\ of\ displaced\ phase} = \frac{k_{rdisplacing}/\mu_{displacing}}{k_{rdisplaced}/\mu_{displaced}} \quad (1)$$

Where,

ג = Mobility

kr = Effective permeability

μ = Fluid viscosity

Mobility ratio strongly depends on the sweep efficiencies. If the mobility of the displacing phase is much greater than the mobility of the displaced phase, the phenomenon called viscous fingering can take place.

Mobility ratios are considered as "favorable" or "unfavorable." A favorable mobility ratio occurs when we have $M \leq 1$; this means that the displacing phase has a less mobility than the displaced phase. An unfavorable mobility ratio $M > 1$ is the other way around. In practical terms, a favorable mobility ratio means that the displaced phase can move more quickly through the reservoir rock than the displacing phase.

Favorable mobility can be achieved by:

- Reducing the viscosity of oil
- When effective permeability to displaced fluid increases
- When effective permeability to the displacing fluid decreases

Figure 1 below represents the effect of mobility ratio on the sweep efficiency. Viscous fingering can occur in unfavorable mobility ratio while when the mobility ratio is favorable displacement is quite efficient**.**

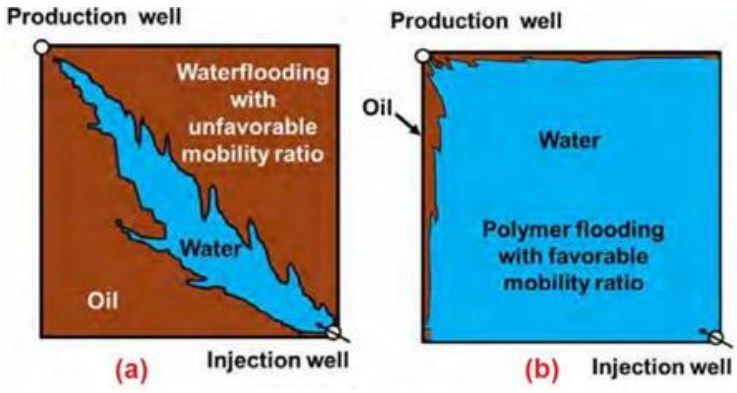

Figure 1: Mobility Ratios a) Unfavorable and b) Favorable [9]

1.4.2 Capillary Number

It can be defined as the ratio of viscous forces to capillary forces [1].

$$Nc = \frac{Viscous\ Forces}{Capillary\ Forces} = \frac{V\mu}{\sigma cos\theta} \quad (2)$$

Where,

N_c = Capillary Number

μ = fluid viscosity

V = pore velocity

σ = interfacial tension between the fluids

θ = Contact Angle

Reducing the oil viscosity or decreasing the interfacial tension (IFT) increases the capillary number, and decreases the residual oil saturation.

1.5 Chemical EOR Methods

Chemical EOR Methods are usually applied in tertiary mode when we want to recover the remaining oil that is left over after the secondary recovery. Chemical processes refer to those processes in which chemicals are added to the fluids to obtain a favorable mobility ratio. While doing chemical flooding process, we expect the chemicals to affect the following;

- Reduce the mobility contrast between crude oil and displacing fluid
- Reduce the interfacial tension
- Increase the Capillary Number
- Solubilization of released oil
- Changes the wettability towards more water wet

1.5.1 Polymer Flooding

Polymer flooding is an EOR technique that utilizes the addition of Polyacrylamide or "Pam" to the water, which increases the viscosity of water significantly and hence improves the sweep efficiency and also the recovery. Polymer flooding makes the oil recovery more efficient by reducing the water/oil mobility ratio, diverting the injected water from the thief zones and through the effects of polymers on fractional flow.

Benefits of polymer flooding include improved oil recovery, increased sweep efficiency and significantly less water required when compared with typical water-flooding & steam injection.

1.5.2 Surfactant Flooding

An enhanced oil recovery process in which a small amount of surfactant is added to an aqueous fluid injected to sweep the reservoir. The presence of surfactant reduces the interfacial tension between the oil and water phases and also alters the wettability of the reservoir rock to improve oil recovery.

Surfactant flooding is used where upgrading of heavy crude oil is required, high permeability and porosity regions, good source of high quality water is available and reservoir temperatures are less than $300^{o}F$.

1.5.3 Alkaline Flooding

The main mechanism of alkaline flooding is to create a reaction between injected alkaline chemicals and crude oil. The reaction forms surfactants which can reduce interfacial tension, alter the formation wettability, and result in emulsification of oil.

In alkaline flooding mechanism, alkaline chemicals, such as, carbonate or orthosilicate of sodium or hydroxide are injected in the reservoir in the slug form. These alkaline chemicals create a reaction with the acid components of the crude oil and produce the surfactant inside the reservoir. Main mechanism is the IFT reduction. For carbonate reservoirs, alkaline flooding is not recommended due to abundance of calcium. Hydroxide precipitation produced due to the mixture between alkaline chemical and the calcium ions may damage the formation.

1.5.4 Alkaline Surfactant Polymer Flooding

Changes in wettability are caused by alkalis, however, for wettability alterations large concentrations are required. If the acid content of the crude oil is relatively high, alkaline flooding gives good efficiency. The process was modified by the addition of surfactant and polymer to the alkali solution that gives rise to a new EOR method known as Alkaline-Surfactant-Polymer (ASP). This method has shown to be an effective, less costly form of micellar polymer flooding.

ASP flooding is rather new technology and laboratory investigations are being done as well as field tests are also being evaluated. In this method, mainly three chemical formulations are utilized alkali, surfactant and polymer solutions.

1.5.5 Viscoelastic Surfactant Flooding

In the recent years, viscoelastic surfactant (VES) flooding has gained much importance in cEOR. Many research papers have been published in this area focusing on the recovery and displacement efficiency obtained by using VES. They are dual in nature and possess the qualities of both polymers and the surfactants. All non-Newtonian are visco-elastic that

they combine with both elastic and viscous properties. It mobilizes the oil in the reservoir by keeping the mobility ratio favorable and by reducing the IFT of the reservoir. Wang et. al., (2010) described that for the same capillary number, displacement efficiency and recovery factor are comparatively higher if the viscoelastic fluid is used as the driving fluid rather than the Newtonian fluid [10]. Viscoelastic Surfactant with excellent thermal stability and resistivity to salinity and divalency could significantly enhance the recovery in carbonate reservoirs. Stability of the chemicals is major issue while employing cEOR. The problem using polymer flooding and surfactant flooding is that most of the polymers degrade at high temperatures, and the surfactant tends to precipitate upon exposure to divalent cations and will partition to the oil phase at high salinities. Viscoelastic surfactant flooding is the better option because it has chemical formulations of both polymer and surfactant and together they improve oil recovery from the reservoir.

1.6 High Temperature and High Saline Carbonate Reservoirs

Middle east reservoirs are usually characterized as high temperature and high saline (HTHS) reservoirs. It is reported that less than 20% of chemical EOR projects were conducted in carbonate reservoirs, especially in the Middle East, where few small-scale pilots were tested [11] and [12]. Middle East carbonates are highly heterogeneous and have complex pore characteristics with wettability variation from mixed to oil-wet [13]. The reservoir conditions within this region can be summarized as HTHS conditions. Carbonate reservoirs are usually characterized as low permeability matrix with fractures, while a considerable portion present high permeability matrix with fractures.

1.7 Heavy Oil Reservoirs

Global heavy oil resources in carbonate rocks have been estimated to be on the order of 1.6 trillion barrels [14], of which about one-third may occur in the Middle East. Productive heavy oil carbonate fields can be grouped into two categories: 1) low matrix permeability, fracture dependent and 2) matrix permeability dependent production. Current worldwide supply and demand dynamics, coupled with the dramatic escalation of crude prices beginning in 2003, has brought a renewed interest in heavy oil (HO) and bitumen deposits. Wafra occur on the broad anticlinorium of the N-S trending Kuwaiti Arch and have good poro-perm characteristics and are not heavily influenced by fractures [15]. A pilot steam flood commenced in February 2006 at Wafra and is ongoing.

1.8 Wafra Ratawi Field

The Wafra field is located in the Partitioned Neutral Zone (PNZ) between Kuwait and Saudi Arabia (Figure 2). Ratawi Formation is a significant hydrocarbon reservoir in many parts of the Middle East. Ratawi formation has traditionally been divided into an upper Ratawi Shale member and a lower Ratawi Limestone member, with the latter being the main exploration target. Major discoveries were made in the lower part of the Limestone member (then termed the Ratawi Oolite) at Wafra Field in 1953. The field produces oil from the Ratawi Oolite reservoir, which has been under production since 1956. By 1988, the average reservoir pressure had declined to nearly half of the initial reservoir pressure after production of almost 600 MMBO. Production curtailment was being considered as an alternative to reduce the pressure decline [16]. The field was shut-in during the first Gulf War and was then brought on-line shortly thereafter with extensive development drilling.

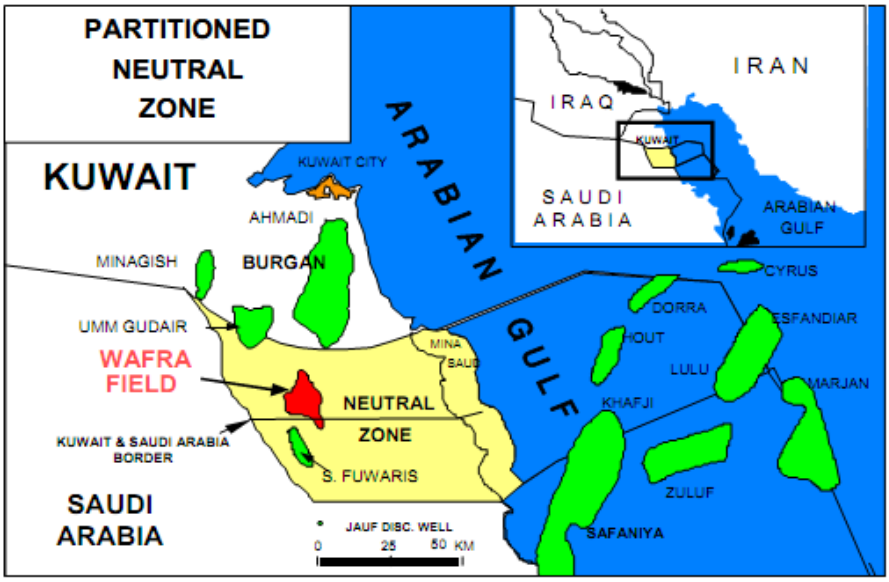

Figure 2: Wafra field location in the Partitioned Neutral Zone between Kuwait and the Kingdom of Saudi Arabia. (SPE 127816)

Liquid withdrawal over the years has depleted reservoir pressures in some parts of the field, leading to a decline in production.

The field is now operated by Saudi Arabian Chevron (SAC), a 100% owned subsidiary of Chevron, and Kuwait Gulf Oil Company (KGOC). SAC operates the field on behalf of the Kingdom of Saudi Arabia under a 60 years concession agreement signed in 1949 that was recently extended in 2009.

1.9 Problem Statement

All previous work on VES as potential EOR fluid lack clear explanation of high adsorption rate on carbonate rock and the mechanism of buildup/break of viscosity in presence and absence of oil. The high pressure drop during core-flooding experiment has not been studied well and how it might affect permeability.

The Ratawi field has exceptionally high levels of divalent cations and the main objectives of this project are to identify the best VES based formulation suitable for cEOR application in Ratawi Oolite reservoir in the Wafra-Ratawi field. Particularly, this study aims at addressing the technical challenges related to applying cEOR to the Wafra-Ratawi reservoir.

1.10 Research Objectives

The proposed research project has the following specific objectives:

1. To determine the interfacial tension of VES and VES/CA systems.
2. To determine the thermal stability of the VES systems in sea water.

3. To study the adsorption of VES on real reservoir carbonate samples.
4. To test the compatibility of the potential VES, and VES/CA systems by combining VES with chelating agent.
5. To perform core flooding and evaluate the performance of the optimum VES systems in carbonate rocks.

Our objective in the work is to explore and optimize VES, or VES-chelating agent (VES/CA) systems as novel EOR methods in carbonate reservoirs. The introduction of VES/CA is suggested to balance the effect of divalent salts on VES. Chelating agents are known for their affinity to salts. Their use would likely reduce the impact of the very high levels of divalent salts on VES (salt balance).

1.11 Thesis Organization

The thesis consists of six chapters. In the first chapter, introduction and importance of EOR is highlighted. Followed by oil recovery methods and categorization of EOR the basic mechanisms of EOR are stated. Different cEOR methods are also discussed. Carbonate reservoirs challenges toward high temperature and high saline environment are elaborated. Then brief introduction about the Wafra Ratawi Field is discussed. After that the problem statement is defined and the objectives are mentioned that are intended to cover in this thesis.

In chapter two, detailed literature review is given for major research on viscoelastic surfactant. Reduction in IFT and increase in capillary number are discussed. Polymer flooding and surfactant flooding literature is reported. After that literature on adsorption, zeta potential and core flooding is included.

In chapter three, all the equipment and materials used in the current study are summarized with the working principle and mechanisms. All the major and the minor equipment and their details are described.

In chapter four, research methodology is described. Description of all experimental procedures followed to achieve the objectives of the thesis are discussed. Procedure for preparing solutions, density and viscosity measurement procedure, IFT, thermal stability, adsorption zeta potential and core flooding procedures are elaborated in detail.

In chapter five, results and discussions are discussed in detail. Results of rock characterization, oil characterization are explained. Then the results of IFT for VES and VES-CA systems are interpreted. Thermal stability of VES system is evaluated with short and long-term aging. Adsorption and Zeta potential results are explained for further evaluation of the VES and VES-CA systems. At the end core flooding results are discussed with detailed analysis of all the parameters and effluent analysis.

Chapter six summarizes our conclusions and recommendations. Outcome of the research in evaluating both systems is discussed.

CHAPTER 2

LITERATURE REVIEW

Over the last few decades the production from the oil reservoirs has been declining and world is focusing on other methods of recovering the oil. Enhanced Oil Recovery is becoming a popular technique to recover the remaining oil from the mature fields. Consequently, oil price keeps rising which makes variety of expensive EOR processes a feasible one to recover the remaining reserves. The one main aim of any EOR technology is to increase the capillary number, so that the discontinuous residual oil could be mobilized and the relative permeability of oil could be improved**.** The other aim of EOR technologies is also to decrease the mobility ratio to avoid fingering and facilitate better sweep efficiency.

Shen (2002) states that cEOR is basically done to reduce IFT, increase capillary number, enhance the microscopic displacement efficiency, improve the mobility ratio and increase the macroscopic sweep efficiency [4]. Lake et al. (1989) described cEOR processes as, "tantalized the industry with promises of significantly improved recovery and gained attention in 1980's" [17]. The aim of cEOR methods is to increase the capillary number. Polymer flooding increases the capillary number by increasing the viscous forces while surfactant flooding reduces the IFT between oil and formation water/injection water. So, the combination of surfactant and polymer named as SP flooding combines the benefit of both.

Generally, cEOR methods cannot be applied to deeper reservoirs because the high temperature and salinity cause the degradation of chemicals. Miscible flooding has been applied for reservoirs deeper than 9,000 ft. Also, cEOR is not suitable for heavy oil recovery due to mobility ratio between the displacing fluid and displaced fluid. Thermal methods are applicable in the reservoirs whose oil viscosity is above 150 cP. Also, carbonate reservoirs are not the favorable candidates for cEOR mainly because of high salinity, temperature, low injectivity, fracture, tight matrix etc. most of the conventional surfactants are susceptible to high salinity, high temperature etc.

The aim of this research is to extend the applicability of cEOR to high temperature and high salinity reservoirs. Among the chemical methods, polymer flooding has been applied largely. Some of successful polymer projects include Daqing Oil Field (China), Marmul field (Oman), North Burbank unit (USA), Sanand field (India). Wang et al. (2009) described that polymer flooding has been widely used for EOR operations in China too [18]. Green et al. (1998) suggested that surfactant can be combined with polymer to do SP flooding [1]**.** The polymer makes the viscosity of displacing fluid closer to oil to achieve favorable mobility ratio. Hirasaki et al. (1974) observed that injecting surfactant alone causes the relative permeability of water to increase and it is balanced by decreasing the aqueous mobility with polymer [19]. The combined flooding process can increase both displacement efficiency and mobility control. Alkali and surfactant can also be added to the polymer to conduct ASP flooding. Katsanis et al. (1983) investigated that alkali can react with minerals such as silicate minerals, alumina silicate minerals, and calcium and magnesium compounds to form scales [20]. Fu et al. (2004) recognized that scale formations and stabilized emulsions made people more attracted in the surfactant-polymer

technology [21]. Usually surfactant helps in reducing the IFT to ultra-low value thereby increasing the capillary number up to 10^{-2} m N/m. Oil Industry has witnessed the use of surfactants for more than 80 years. De Groote (1930) used polycyclic sulfonate and wood sulfate in 1920's to improve oil recovery [22].

Hirasaki et al. (2008) observed that the surfactants used in 1960's were made either by direct sulfonation of aromatic groups or by organic synthesis of alkyl/aryl sulfonate [23]. In 1970s, an extensive research and field testing was triggered by the anticipated increase in oil price. Taber (1969) and Melrose (1974) recognized that capillary number controlled the amount of residual oil remaining after flooding by conducting extensive series of studies [24], [25]. General revelation from these studies stated the reduction of IFT from 20-30 mN/m to 0.001-0.01 mN/m leads to the lowest residual oil saturation.

Gale and Sandvik (1973) proposed four criteria for selecting the surfactant for EOR process: low oil–water IFT, less adsorption, compatibility with reservoir fluids and low costs [26]. Recently, Zhu et al. (2013) investigated the applicability of the following methodologies to screen and design the surfactants capable of providing ultra-low IFT [27].

- Hydrophilic- Lipophilic balance (HLB) values
- R-ratio (ratio of interaction energy of surfactant with oil to surfactant with water in interface layer),
- Molecule Geometry Packing Parameter and
- Quantitative Structure- Property Relationship.

Pye developed the easy solution to control the water mobility by using water soluble polymers such as PAM (polyacrylamides) [28]. Since then, synthetic and bio polymer

applicability along with other methods became popular in EOR technologies. But it was found that injecting polymer is not the best option always. It has limitation such as degradation, poor stability, compatibility, inability to access low pore volume, low injectivity. Seright (1983) studied the susceptibility of the polymer to detrimental effects caused by high temperature and high salinity commonly found in reservoirs. Carbonate reservoirs are usually characterized with high temperature and high salinity [29]. However, in our case the temperature is moderate, and the salinity is high.

Levitt et al. (2008) conducted the following experiments to select a polymer for use in SP flooding: (a) Polymer hydration, (b) Filtration, (c) Compatibility of Polymer and Surfactant, (d) Viscosity, (e) Chemical stability, (f) Degree of hydrolysis, (g) Calcium tolerance, (h) Thermal stability, and (i) Core flooding [30]. SP flooding provides lower residual oil saturation and lower mobility ratio. Gao et al. (2010) evaluated SP flooding potential and stated from industrial experience that the following criteria should be met before developing SP flooding [31]:

- The oil gravity is greater than 25 $°API$.
- Light intermediates are desirable and oil saturation is greater than 30 % .
- Depth of the reservoir should be less than 8000ft and reservoir temperature should not exceed 175°F.
- Formation permeability more than 20mD and net thickness more than 10ft
- Sandstone is preferred.

Manrique (2010) demonstrated that most of the cEOR applications were in sandstone reservoirs [32]. Less than 20% of the cEOR projects were conducted in carbonate reservoirs, in which 64 polymer flooding projects and 6 SP projects were reported. Few

case studies were reported in detail and most were listed in statistical reports. Manrique, et al. summarized the EOR experience in carbonate reservoirs [11]. They identified miscible gas injection as a feasible method in such low permeable reservoirs to overcome low injectivity. He found that chemical methods contribute marginally in terms of overall recovery**.** They realized that if the chemicals are stable enough, at high temperature/high salinity/high divalency, cEOR could significantly enhance the recovery in tight carbonate reservoirs. Morvan recently evaluated VES with excellent thermal stability and resistivity to salinity and divalency [33]. Adams and Schievelbein (1987) demonstrated that although no extensive field case studies for cEOR in carbonate reservoirs are available, carbonate reservoirs can be chemically flooded [34]. Austad and Milter (1997); Hirasaki and Zhang (2004); Seethepalli et al. (2004) used various kinds of surfactants (cationic, anionic, non-ionic and amphoteric) for such an application in low permeable carbonates [35], [36], [37]. Natural fractures are more common in carbonate than in sandstone. High density of fractures; high permeability zones, and low matrix permeability zone lead to the uncertainty of fluid flow in carbonate reservoirs. Presence of these fractures and diversified zones tend to complicate the EOR applications in carbonate reservoirs.

Ehrenberg and Nadeau (2005) studied that carbonate reservoirs rocks are usually characterized by the low permeability matrix with high fractures [38]. Hence, Injectivity becomes an easy problem with any reasonable concentration of polymer in such Carbonate reservoirs. Also, carbonate reservoirs contain high concentration of divalent ions which hinder the applicability of conventional SP systems. Most of the carbonate reservoirs are also characterized by high temperature and salinity. Surfactant alone cannot be applied without effective mobility control. Mobility control process is aided by injecting polymer.

Han et al. (2013) studied that particularly in Middle East, applicability of chemical EOR in carbonate reservoirs is complicated by high temperature and salinity [39]. At high temperature, the stability of chemicals particularly polymer gets affected. At high temperature, the surfactant tends to precipitate upon exposure to divalent cations and will partition to the oil phase at high salinities. These carbonate reservoirs require specially formulated chemicals system which could mitigate the above problems. Employing VES in our system was sought to address these problems. All viscoelastic fluids combine both elastic and viscous properties. When the time scale of flow (t_f) is much less than the relaxation time (t_r) of the viscoelastic material, elastic effects dominate. It leads to the increased displacement efficiency. On the other, if the relaxation time is smaller than the flow time, then the viscous forces dominate which could give better mobility control. Weissenberg number is the ratio of relaxation time (t_r) to flow time (t_f). This dimensionless number is named after Karl Weissenberg, a pioneer in the field of non-Newtonian fluids.

Jennings et al. (1971) and Frank et al. (1970) observed that previously in polymer flooding, the viscoelasticity of polymer was ignored by many researchers [40], [41]. A lot of authors have done investigation on the effect of viscoelasticity on the polymer sweep efficiency and presented laboratory results during cEOR. Wang et al. (2000) stated outcomes of core flooding with viscoelastic polymer solutions indicating that sweep efficiency increases with the elastic properties of the injected fluids [42]. Xia et al. (2004) and Wang et al. (2007) also investigated the impact of viscoelasticity of the polymer solutions [43], [44]. All authors across the world suggested that in comparison to water flooding and polymer flooding, a field proven polymer flooding method using high concentration viscoelastic

polymer solution could result in higher recovery. This is because of the high elasticity of the polymer solution which results in increased sweep efficiency. Urbissinova, et al. (2010) studied the effect of elasticity alone during VES/P flooding and reported that wider distribution of the polymer molecular weight increases the elastic properties which provide the extra resistance for the polymer flow in the reservoir and in turn more oil was recovered and less oil was trapped as residual in the reservoir [45]. They stated that by increasing the MWD of the polymer solution, polymer sweep efficiency could be enhanced. Wang et al. (2011) reported that more than 20% OOIP compared to water flooding can be achieved by injecting higher concentration of polymer [18]. However, injecting such higher concentration possesses injectivity problems. Hence, Injectivity becomes a problem with such high concentration of polymer in such carbonate reservoirs.

Wang et al. (2000) reported an additional increase of oil recovery (7-14% of OOIP) after polymer flooding in Daqing Oil Field [42]. Wu et al. (2007) discussed the displacement efficiency of the polymer injection from the perspectives of the capillary number and the viscoelasticity [46]. Xia (2008) studied the EOR mechanism of polymer solution from a microscopic perspective and found that large micro force during polymer flooding results in higher displacement efficiency [47]. Ranjbar et al. (1992) studied the quantification and optimization of VES effects of polymer solutions for EOR and found that an index based on Maxwell-Fluid-Relation is used for quantifying the viscoelastic behavior of polymer solutions in porous media and not the usual relaxation time [48].

Wang et al. (2010) suggested that for the same capillary number, displacement efficiency and recovery factor are comparatively higher if the viscoelastic fluid is used as the driving fluid rather than the Newtonian fluid [10]. They studied the micro forces in pores causing

the displacement efficiency during flooding. They concluded that flow lines of viscoelastic fluid in pores are different than flow lines of Newtonian fluids. Flow lines look like expanding and contracting with viscoelastic fluids. Presence of micro forces in pores is larger for viscoelastic fluids than Newtonian fluids. Among the properties, first normal force differential and Weissenberg number affect the shape of the flow lines and affect displacement efficiency.

Xia et al. (2008) studied the effect on residual oil caused by micro forces during chemical flooding [47]. They conducted extensive experiments to study the influence of elastic characteristics of the driving fluid on displacement efficiency. They concluded that micro forces are the main reason for recovery of residual oil and mobilizing it. They showed that the micro forces acting on the residual oil increase with increased elasticity. Further, it could result in increased displacement efficiency for viscoelastic displacing fluids at constant pressure gradients conditions.

Wang et al. (2001) studied the displacement mechanism of viscoelastic polymer solution. They concluded that the higher the viscoelastic characteristic nature, the higher the displacement efficiency [49]. Yin et al. (2012) studied the characteristics of flow for viscoelastic polymer solution using finite volume method in expansion, contraction and expansion contraction channel [50]. They indicated that the elasticity of the polymer solutions is proportional to the polymer velocity, the micro scale sweep efficiency and the flowing area and thus they interpreted that sweep efficiency could be improved. Wang et al. (2013) developed the new simulation model for viscoelastic polymer flooding by incorporating the displacement efficiency due to the elastic nature along with viscous nature [51].

But exploiting the viscoelastic nature through injecting high concentration of polymer may not be an ideal option for carbonate reservoirs characterized by low permeability. Injectivity becomes a severe issue. Weissenberg number has been used to characterize the elastic properties of viscoelastic fluids. So, surfactant possessing viscoelastic properties were used. Degre et al. (2012) reported that VES technology has been developed to match the rheological properties of the polymer solutions in a wide range of temperature and salinity without posing injectivity problems [52]. Ehrenberg and Nadeau (2005) described that carbonate reservoir rocks are usually characterized by the low permeability matrix with high fractures [38]. Morvan et al. (2009) reported that VES solution can mobilize significant portion of the residual oil [53]. Morvan et al. (2012) concluded that higher Weissenberg number could be attained by using VES at lower shear rates without posing injectivity problems [33]. This technology was patented in 2008 by Rhodia.

Recently, new perception about the potentiality of VES through extensive lab studies has come to light. Boyer et al. (2005) discussed that VES had been a part of a successful field applications in low permeable rocks as in Hydraulic fracturing [54]. Experiences from these applications demonstrate the positive enhancements during stimulation process which makes VES an option to try in other parts of Oil Industry such as in EOR.

Samuel et al. (1997) indicated that VES can have rod like micelles that gives high viscosity value when salts added to the solution [55]. Huang and Crews (2008b) discussed that the best VES can provide stable viscosity up to 250°F with the addition of a stabilizer in the form of nano particles [56]. It can increase the viscosity of the fluid. Cates (1987) observed that entangle micelles solution exhibits the complex rheological profile [57]. Lakatos et al. (2007) reported a recent laboratory study stating that 10% incremental production could be

achieved by VES [6]. But the surfactant mixture they have used was highly affected by salt concentration in solution and it only can be used in low salt concentration environment. Morvan et al. (2009) proposed the use of VES for high saline reservoirs [53]. Further, the injectivity issue commonly associated while using high concentrated polymer to aid the displacement efficiency was mitigated by employing VES. More recently, Zhu et al. (2013) found that high viscoelasticity of SP flooding is an important factor contributing to the higher recovery [27]. It is expected that the major drawback of VES is its high adsorption. Since VES has no memory effect, the adsorption becomes permanent unlike in polymer. Mahmoud et al. (2015) investigated the chelating agent role in EOR processes in carbonate and sandstone reservoirs. The chelating agent proved to work well in saline environment [58].

Lakatos et al. (2007) studied VES as the mobility control agent in low tension surfactant floods [6]. The viscoelastic surfactant influenced the IFT at the low concentration range. The positive effect due to it is that formation of wormlike micelles starts at very low concentration contrarily smaller CMC does not mean effective solubilization as in the case of conventional surfactants. VES influences the IFT at the lowest concentration but the IFT lowering is not sufficient to increase the mobility of the residual oil after secondary recovery processes. No memory has been observed while injecting VES. Irreversible adsorption of VES can happen. VES improves both microscopic displacement efficiency and provides effective mobility control. Multicomponent injection strategy was not recommended for VES along with other surfactants.

Wu Wenxiang et al. (2007) studied the surfactant and viscoelastic polymer system for sandstone reservoirs [46]. They reported the importance of first normal stress difference in

higher recovery if the viscoelasticity of the polymer is high. Also, they noted the displacement plays a significant role than sweep efficiency in improving the recovery. An interesting point they have concluded is even with higher IFT, displacement efficiency could be more due to the elastic nature.

Mariyamni et al. (2012) studied Wormlike micelles (WLM) applicability as the mobility control agent [59]. Thermal stability and chemical compatibility conducted by them revealed that WLM could withstand high divalent ions concentrations. Carbonate reservoirs considered in our study are known to contain more divalent concentrations. Using WLM as the displacing agent will reduce the mobility ratio to 0.029 and additional recovery of 17.6% was achieved.

Youyi et al. (2013) while studying the main factors on oil recovery of SP flooding, they formulated the system KYPAM as the polymer, Sodium petroleum sulfonate and heavy alkyl benzene sulfonate as the main surfactant along with Betaine, sodium alkyl ethoxylate sulfonate and alkyl ether sulfosuccinates [60]. They concluded that if the ratio of viscosity of the displacement fluid to that of oil was more than 2, then higher recovery could be obtained. Additionally, they found that more than 15% of oil recovery is achievable if the IFT lowering is also considered along with the mobility control.

Degre et al. (2011) measured the viscosity of VES at low concentration (0.1% to 0.5%) and concluded that the VES system has positive impact of brine concentration on viscosity and is salt tolerant [52]. Levitt et al. (2008) evaluated thermal stability of viscosifying surfactants at both 51°C and 90°C. There was no viscosity loss observed for 51^{o}C and a maximum of just 10% viscosity loss has been reported at 90°C. The study implied the

better performance shown by VES over the conventional polymer whose hydrolysis exceeds 90% after 100 days. Even 70% hydrolysis may affect tolerability of calcium ions concentration exceeding 5000 ppm [30]. But carbonate reservoirs usually contain high divalent ions. Calcium tolerance is improved for sulfonated polymers having comparable degree of hydrolysis than regular HPAM, but cloudiness could occur if calcium content exceeds 2000 ppm. Zaitoun (1983) reported that turbidity is closely related to plugging behavior making it difficult to use the polymers in these conditions [61]. Further, carbonate reservoirs are characterized with tight matrix. Degre et al. (2011) discussed that viscofying surfactant technologies provide good in depth propagation and can produce more oil than polymer flooding [52].

The usual standard industry criterion claims that polymer flooding is not applicable for oil with viscosities more than 150 cP. But exploiting viscoelasticity could change the fortune. Mogollon et al. (2013) reported that injecting polymer at the concentration of 800 to 1500 ppm could recover heavy oil up to the viscosity of 5000 cP [62]. But still the injectivity could be a problem which could be addressed through fracturing and employing horizontal wells.

Delamide et al. (2012) reported that employing horizontal well for polymer flooding in pelican lake field, could recover highly viscous oil of ranges between 1000 – 2500 cP [63]. They concluded that polymer flooding via its viscoelastic nature has the potential to recover heavy oil. Recently in SP flooding, it was found that usage of VES in the form of amphoteric surfactant along with polymer polyacrylamides could provide effective mobility ratio. Luo et al. (2013) reported that injected amphoteric surfactant increases the viscosity of polymer there by making it an ideal combination to push the heavy oil with

effective mobility ratio. They also reported that SP system they formulated for Western Canadian heavy oil reservoirs exhibited good resistance to hardness (13,600 mg/L) [64].

Levitt et al. (2013) addressed the challenges of cEOR in High Temperature, High salinity, low permeable carbonates [65]. They stressed the importance of low permeable formation which requires optimized polymer molecular weight distribution in order to achieve better mobility reduction and injectivity. They concluded that for low permeable carbonate reservoirs (10-100 mD), optimized injectivity and viscofying power of polymer could be obtained by degrading a medium-MW copolymer. They found through viscosity measurements that degraded moderate – MW copolymer maintained a higher average MW than low-MW copolymer.

Dahanayake et al. (2010) realized that to increase the capillary number, surfactant or polymer alone individually does not suffice [66]. Also, the conventional SP flooding was expensive and possesses limitations in terms of compatibility, formation damage etc. So, they claimed that VES is capable of providing both displacement and sweep efficiency and considered as the single flooding fluid. They formulated the single flooding fluid with 1% of non-polymeric VES in water with salinity of 20 lb/1000 gallons. They were able to achieve IFT of less than 1 mN/m and viscosity of about 10 cP. They selected the VES from the group of cationic, amphoteric, zwitterionic, and anionic or the combination of all. The non-polymeric VESs they used were viscoelastic even at 350^{o}F and higher salinity. They also reported that non-polymeric surfactants that form viscosifying fluids are advantageous because they are of low molecular weight than polymers. They promptly reported that the extent of viscosity increase will vary depending on the surfactant type, brine content in the flooding fluid and in the formation, composition of oil etc. Another advantage of VES is

that they remain stable in high shear applications. Also, fluids containing VES have conductivity in the reservoirs. They suggested that non-viscoelastic surfactant can be added to the VES to enhance better IFT reduction and mobility control. It was also reported that concentration of non-viscoelastic surfactant could be as low as 0.1%.

Dahanayake et al. (2012) extend the applicability of VES to carbonate reservoirs [67]. They claimed that VES could effectively plug the high permeable fracture and then VES could permeate in to high porous matrix. The viscous gel compatiblizers with the oil entrapped. They claimed that aqueous gel with VES should be injected into the reservoir for three to five days. Then the residence time of few days could be allotted and then production could happen for 10 days. They suggested that they can inject the fluid at low shear rate, but still it could generate huge viscosity within the reservoir upon the relaxation of shear. They also reported that polymer could be added to enhance the sweep efficiency of VES and surfactant could be added to enhance IFT reduction.

From all the above there is a potential for using VES or VES with surfactant in cEOR. Mahmoud et al. (2013) introduced the effect of high pH chelating agent as novel solution of chemical EOR [68].

The use of chelating agents for EOR applications depends on capturing cations from injected water and from the formation brine and this will force the rock surface to release more cation to achieve equilibrium. In addition, capturing cations from the connate water and the rock will change the surface properties of the rock like wettability through promotion of ion exchange. The number of chelated cations depends on pH value of the fluid. As the pH value increases the number of chelated cations from the rock increases.

The rock dissolution process will force the rock to release some oil that attached to the rock surfaces and this will increase the oil recovery. Some of the chelating agents used in the oil industry are shown in Figure 3**.**

Flooding with high pH fluid is expected to change the wettability of the rock to more water-wet. Rossies et al. (2010) reported that the pH value of the solution and the oil composition affects the wettability of sand grains to be oil-wet or water-wet [69]. Mahmoud et al. (2013) mentioned that chelating agents chelates cations from the rock and due to that the density and viscosity will increase causing increase in the pressure drop with time until no more chelation of cations [68]. The chelant will complex metal ions from sea water, formation water, and rock surfaces forming complex structure with high density and viscosity. The increase in the injected fluid viscosity will improve the displacement efficiency and will enhance the mobility control. In the enhanced oil recovery, these fluids will be used at low concentration (maximum 5 wt.%), therefore the improvement in permeability will not be as in the case of the stimulation but at least it will not cause formation damage and keep the permeability at a constant value or slightly will improve it.

The effects of EDTA chelating agent on the zeta potential of Berea sandstone are presented in Figure 4. Attia et al. (2014) observed that Na_4EDTA solution with low salinity water (Arabian Gulf water diluted 10 times) decreased the zeta potential of Berea sandstone more than the low salinity water and the deionized water [70]. When Na_4EDTA concentration increased from 1wt% to 5wt% the zeta potential of Berea sandstone decreased from -33 to -25 mV. Ramez et al. (2011) studied the relationship between the zeta potential value and the oil recovery for the same fluid [71]. They found that as the salinity decreased the negative value of the zeta potential increased and the oil recovery increased. This indicates

that chelating agent is preferred to be used than low salinity water to improve the oil recovery. Attia et al. (2015) conducted core flooding experiments given in Figure 5 that showed that the 5 wt % Na_4EDTA of pH of 12.2 injected after sea water flooding resulted in additional oil recovery from the Berea sandstone cores of about 30% of the initial oil in place [72].

Therefore, these combinations of VES and VES/CA will be explored and screened to identify the system that suits Wafra-Ratawi reservoir conditions and fluid properties. The aim of this research is to extend the applicability of cEOR to high salinity and heavy oil reservoirs.

Surfactant adsorption is a phenomenon on solid−liquid interfaces where transport of surfactant molecules from the bulk phase to the interface occurs. Paria (2004) and Zhang (2006) explained this process as the interface is energetically favored by the surfactant compared to the bulk phase [73], [74].

Kamal (2015) investigated the effect of gemini surfactants and their potential applications in the enhanced oil recovery [75]. Evaluation of different surfactants was done by rheological characterization and interfacial tension, the two important parameters for the selection of chemicals. Also, wettability alteration, adsorption and various other parameters that effect the performance were investigated.

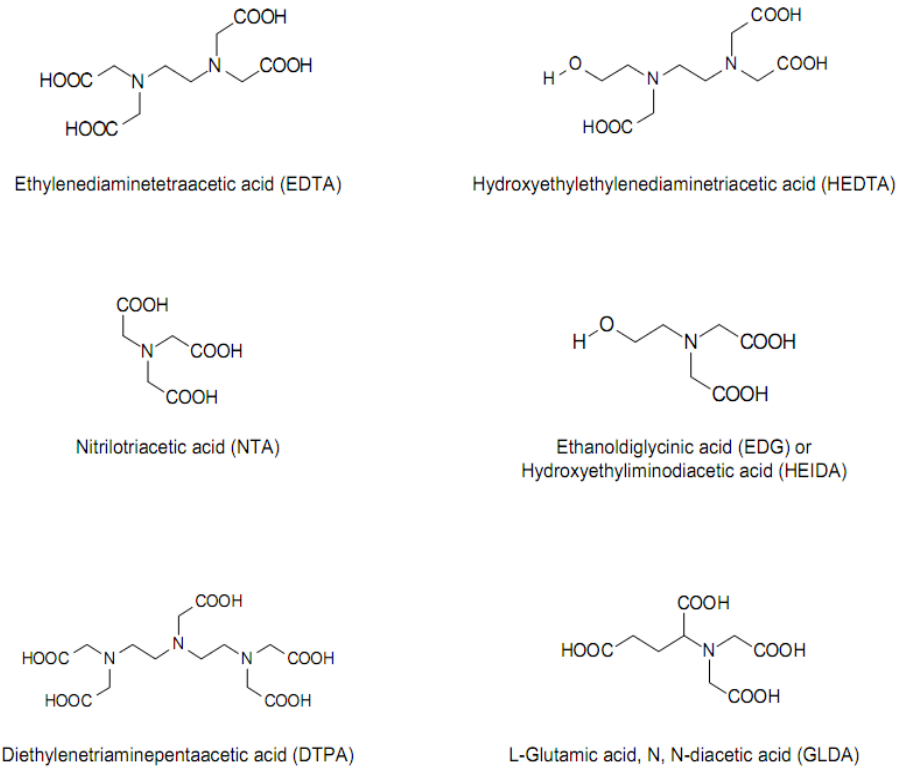

Figure 3: Chelating agents used in oil industry

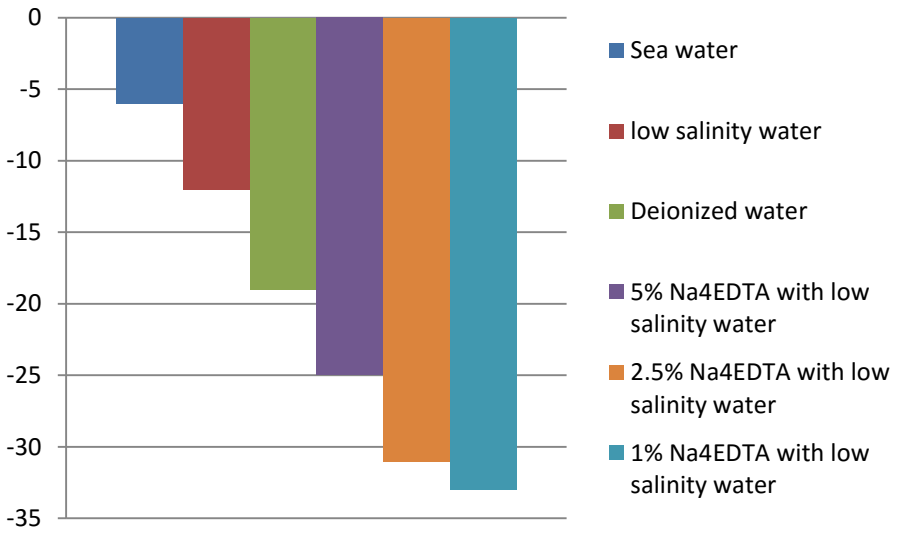

Figure 4: Variation of Zeta potential of Berea sandstone with different solutions [70]

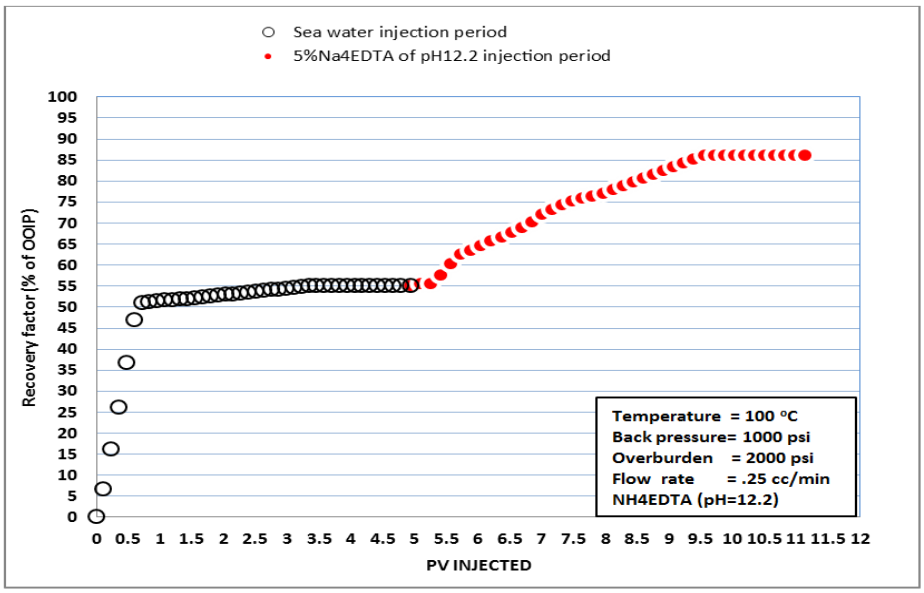

Figure 5: Oil recovery achieved from Berea sandstone core flooded with sea water and 5% Na_4EDTA solution of pH 12.2 [72]

Kamal et al. (2015) studied amphoteric and anionic surfactants for the application in chemical EOR [76]. They evaluated the thermal stability and the interfacial tension of the surfactants. Thermal stability was measured with TGA, FTIR and NMR. They evaluated that surfactants were stable for short exposure times. Structural changes were found when the long term thermal stability was done. While interfacial tension is decreased initially and then increased by the increase in surfactant concentration. Also with the increase in temperature the IFT was increased which was reduced by the addition of salts.

Ahmadi et al. (2012) highlighted the adsorption equilibrium of the combination of different types of nanosilica and Zyziphus Spina Christi, a novel surfactant, in aqueous solutions for EOR and reservoir stimulation purposes [77]. They utilized the conductivity technique to assess the adsorption of the surfactant and nanosilica in the aqueous phase. Batch experiments were used to understand the effect of adsorbent dose on sorption efficiency as well. The adsorption data were examined using four different adsorption isotherm models (Langmuir, Freundlich, Temkin, and Linear), and the adsorption parameters were determined for each model. This study suggested that a Freundlich isotherm model can satisfactorily estimate the adsorption behavior of combination nanosilica and surfactant adsorption on carbonates. They showed that their results can help in appropriate selection of surfactants in the design of EOR schemes and reservoir stimulation plans in carbonate reservoirs.

Solairaj et al. (2012) studied the dynamic surfactant retention of anionic surfactants of all types for a wide range of conditions and found similar results for sandstone and carbonate rocks [78]. They measured the retention for both the surfactant polymer (SP) and alkaline surfactant polymer (ASP) and found the values in between 0.01 to 0.37 mg/g-rock. They

correlated different parameters like acid number of oil, pH, temperature, salinity, mobility ratio, co-solvent concentration and surfactant molecular weight. They utilized HPLC measurements to measure the surfactant concentration in the coreflood effluent samples.

Amoudi et al. (2016) studied fluorosurfactant and polymer formulations for EOR in carbonate reservoirs. They investigated interfacial tension, rheological properties, thermal stability and adsorption on the rock surface [79]. The effects of the surfactant type, surfactant concentration, temperature, and salinity on the rheological properties of the SP systems were examined. At 90^{o}C both surfactants were found thermally stable. Out of two they utilized the best for interfacial tension, adsorption and core flooding experiments. Core flooding results reported in this study gives additional oil recovery of 42%.

Alvarez et al. (2014) carried out a study on adsorption of zwitterionic surfactant (cocamidopropyl hydroxysultaine) to measure the static adsorption [80]. They utilized limestone and HPLC method for their experiments. Three different aqueous media like HPLC water, sea water and connate water and temperature conditions of room temperature and 70^{o}C were investigated. Both HPLC water and seawater, the surfactant adsorption followed a monolayer Langmuir tendency. In contrast, for connate water, the surfactant presented a new adsorption profile, characterized by two regions: (i) At surfactant concentrations below 1500 mg/l, adsorption is increased because the number of divalent cations increases in the aqueous media. Divalent cations usually promote the adsorption of surfactant on the rock by electrostatic forces. (ii) At surfactant concentrations above 1500 mg L^{-1}, divalent cation promotes the transition from micelles to vesicles; the adsorption decreases, giving as a result a decrease in the concentration of monomers, thus reducing the interaction between the surfactant and the rock, and therefore, lower adsorption values

were obtained. They also observed that adsorption is reduced significantly as the temperature is increased because of the exothermic nature of adsorption processes.

Morvan et al. (2009) worked on a new viscoelastic surfactant fluid for cEOR applications [53]. Viscoelastic fluid exhibited a viscous phase at less concentration and high temperature condition, helpful for increasing the oil recovery. Wormlike micelles are generated by self-assembled surfactants. Leng et al. (2006) used a microfluidic device to establish the phase behavior diagram of the surfactant in pure water [81]. They observed isotropic wormlike micelles.

Coreflood experiments were performed in Clashach sandstone at 80°C with brine containing surfactant concentrations. Surfactant was moderately adsorbed on the sandstone and displaced a great amount of residual oil. In core flooding this viscoelastic fluid provided greater viscosity and better mobilization of residual oil with less adsorption. In this work, authors evaluated a lab approach to test and characterize a new VES fluid for cEOR. Detailed characterizations were performed by means of a microfluidic device. It was observed that viscosity is less dependent on concentration of brine, and no big difference when the flow behavior compared in low salinity and in synthetic sea water was indicated. Compared to PAM in hard water, significant viscosity at high temperature was maintained with an exceptional thermal. Adsorption and mobility values were also moderate and the VES fluid showed an increased recovery of residual oil.

Azad et al. (2014) studied that undergoing a chemical EOR process in carbonate reservoirs is a big confront because of the harsh reservoir conditions [82]. Harsh conditions include high salinity, hardness and temperature. In this study three different viscoelastic surfactants

(Ethomin, Armovis and Aquadat) were screened based on Worm Like Miscelles (WLM) growth and IFT. Among the 3 VES being screened at harsh conditions, Armovis exhibited viscoelastic properties at harsh conditions. Armovis needs salts to generate WLM, which is favorable for high salinity carbonate reservoirs. Viscoelastic surfactant increases the sweep efficiency and reduces the IFT based on the growth of WLM. High viscosity is related to the sweep efficiency and IFT is for moving the oil from the pores. They studied the ratio of viscosity and IFT of VES, S/VES and VES/P system with sea water 57,642 ppm and temperature of 70^{o}C. VES as a single system gives higher viscosity/IFT ratio than S/VES and VES/P. VES/P system is better than S/VES system. Adding conventional surfactants to VES arrest its WLM growth. VES can extend the applicability of chemical EOR upon optimal formulations. Further works are in progress. VES can be used as the diverting agent to improve the sweep efficiency in fractured reservoirs. Core flooding with relatively homogenous and heterogeneous fractured core was done to quantify the over estimation of recovery in homogenous core.

Azad et al. (2014) in this work investigated the potential of viscoelastic surfactant (VES) in recovering heavy oil in complex reservoirs [7]. VES exhibits certain unique properties which are ascertained individually. The properties include IFT reduction, viscosity, elasticity, emulsification, salinity resistance, compatibility, and thermal stability. The properties of VES extend its applicability in complex reservoirs and hybrid technique that combined the synergism of VES, P, and hot water had been studied. Reservoir simulation studies with 5-spot pattern were conducted to compare the performance of Steam flood, polymer flood, and hybrid VES flooding in thin heavy oil reservoirs. Results indicated that

VES could be an ideal hybrid option along with hot water to recover high viscous heavy oil in thin reservoirs.

VES self assembles to form Wormlike Micelles (WLM). WLM can grow at favorable conditions generating huge amount of viscosity. VES's resistance to salinity, divalency and temperature can be exploited. VES could form emulsion which could also contribute to the heavy oil recovery. VES also reduces the IFT. VES when combined with polymer could give additional residual viscosity that could contribute to the sweep and displacement efficiency. VES's thermal stability could be exploited to synergize it with hot water. These properties of VES were studied and optimized to enable its applicability in heavy oil reservoirs. Reservoir simulation studies were carried out for complex heavy oil reservoirs. The efficiency of polymer flooding, steam flooding, and VES flooding was compared. Results indicated that VES when applied synergistically with hot water could provide an alternate option to the existing methods for heavy oil recovery.

VES seems to be an excellent commodity for improving the recovery factor in heavy oil reservoirs where conventional methods fail. VES exhibits all the properties that an EOR fluid can provide. Further its compatibility with polymer could address the problem of VES breakage with oil. VES can be valuable part of the hybrid EOR technique if applied properly. VES can be applied in NFR and thin reservoirs as it is a living polymer which can be tuned to our need. Further studies are needed.

Azad et al. (2014) studied that mobility control is the most important phenomenon that contributes to the volumetric sweep efficiency in enhanced oil recovery processes [83]. Polymers have been used by the industry to provide the required viscosity to the injection

fluids. However, applicability of polymers has its limitation. Most of the polymers easily degrade under harsh reservoir conditions. In this work, they investigated the rheological aspect of viscoelastic surfactant (VES) as an alternative to the polymer in chemical EOR processes. VES self assembles at favorable conditions to form wormlike micelles whose length can vary significantly. The conditions ascertained in this work are concentration, shear rate, temperature, time; salinity etc. In addition, the efficiency of VES with the polymer at various conditions was compared. Results indicated that VES can generate higher viscosity at the extreme conditions of reservoirs. This might be beneficial for EOR point of view. Also, the comparative studies confirm the potential of VES over polymer as an EOR fluid.

The main purpose was to study the applicability of VES as an EOR fluid to provide mobility control over wide range of reservoir conditions. Conditions include temperature, time, salinity, concentration and shear rate. The comparative studies between VES and polymer could be used to choose the specific one as a mobility control agent for the prevailing conditions.

Li et al. (2016) studied the displacement efficiency of VES in EOR [84]. A cationic surfactant and a long chain unsaturated amide betaine were mixed together at a certain ratio to achieve VES-JS. It has strong viscoelasticity and has good ability to reduce the oil−water IFT to a low order 10^{-2}∼10^{-3} mN/m. They investigated the effects of reservoir permeability, VES concentration, injection rate/volume/time, and reservoir heterogeneity on displacement efficiency. Interfacial tension and rheological parameters were determined for different concentration of VES. For permeability variation recovery increased at first and then becomes flatten at high values of permeability and there was no obvious effect.

The recovery increased initially by adding different concentrations of VES but after some point if stabilizes and further no more increment in the recovery was obtained. This may be due to disruptive effect of micelle-hydrocarbon interaction and improvement in shearing action. Incremental recovery was obtained by increasing the flow rate but after the injection rate increases to a certain degree, the aggregation structure of VES was broken to make the recovery increment stabilized. Results reported by them indicate that under the experiment conditions, VES flooding can improve oil recovery ratio from 10.64% to 24.72%. They also compared the incremental recovery from polymer and surfactant. VES gives 17.18% while polymer and surfactant gives 10.56% and 8.64% respectively which clearly shows VES has better application in EOR than polymer and surfactants.

CHAPTER 3

EXPERIMENTAL METHODOLOGY AND MATERIALS

3.1 EQUIPMENT

3.1.1 Helium Porosimeter

Helium porosimeter is used to determine the grain volume and pore volume of the core samples collected from Wafra Ratawi Reservoir. The basic principle includes the application of Boyel's law and Charles law expansion of helium gas. Equipment is first calibrated with 1.5" core plugs and then pore volume is measured by placing the sample core inside the hassler type core holder. A data acquisition unit attached to the porosimeter gives the digital output for the samples. Figure 6 shows the helium porosimeter used.

3.1.2 X-ray Diffraction and X-ray Fluorescence

Mineralogical composition is measured using x-ray diffraction and x-ray fluorescence technique. An X-Ray Diffractometer analyzer measures the intensity of x-rays which are diffracted into wave patterns by the atoms in the crystal compounds contained in a sample whereas an X-Ray Fluorescence analyzer measures the intensity of fluorescent radiation given off by the electrons in the various elements. Intensities are measured to determine how much of each element or atoms are present in the sample. Figure 7 below shows the X-Ray Diffractometer analyzer.

Figure 6: Helium Porosimeter

Figure 7: X-Ray Diffractometer

3.1.3 Thin Section Analysis

Figure 8 shows the microscope used for the analysis of the thin sections. Thin sections of the core samples 14 and 79V are prepared. The top and bottom sections of the cores are used for the preparation of specimens. The prepared specimens are examined for the detailed description about the structure and geology of the core samples using microscope. The lens used in the microscope is 500µm. These structures can be used to account for the origins of a sediment, its transport pathways, and the processes of deposition and deformation.

3.1.4 Weighing Balance

Measurement of the weights is done by using the electronic and digital weighing balance that can measure the accurate values upto four decimal places. The measuring pan is inside a transparent enclosure with doors so that dust does not collect inside and also air do not affect the reading from the balance.

3.1.5 Density Meter

Density measurements of aqueous solutions, viscoelastic surfactant solutions, oil and formation water are achieved by using the density meter from Anton Parr DMA 4500 M. Firstly, the tube inside the density meter is cleaned properly using hot water so that there is no contamination left inside. Then our desired solution is injected from the inlet on the right side so that tube completely fills. The standard mode is selected for density measurements. After that temperature values are adjusted to know density at different temperatures. After taking the density measurement, the tube is flushed again with hot water and is cleaned and the waste fluid is collected from the outlet port on the right side of equipment. The density meter is given in Figure 9.

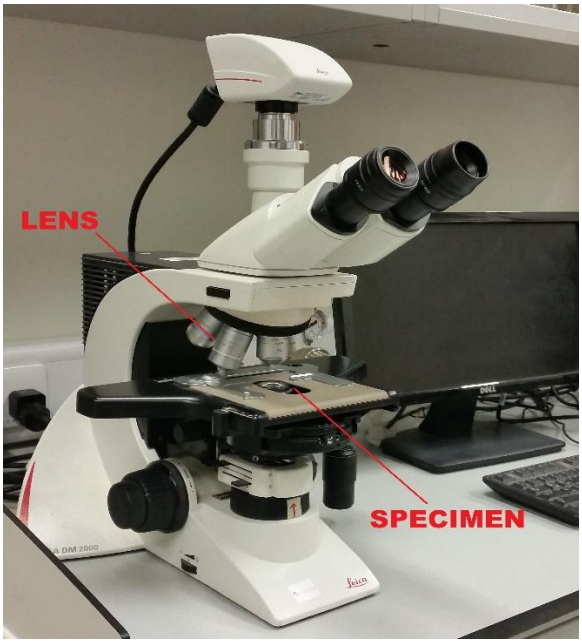

Figure 8: Microscope for Thin Section Analysis

Figure 9: Density Meter

3.1.6 Multi position Stirrer

Figure 10 shows the multi position magnetic stirrer used for stirring the samples. This includes the option of heating as well. Speed of the stirrers can be controlled by a knob dedicated to each stirring position.

3.1.7 HPLC for SARA Analysis

High-performance liquid chromatography (HPLC) by Agilent Technologies 1260 Infinity is used to separate out the heavy oil sample into four chemical group classes, namely saturates, aromatics, resins, and asphaltenes, the so-called SARA fractions. The equipment used for this purpose is Infinity 1260 by Agilent Technologies. A data acquisition system is attached to HPLC for the measurement of the sample. 1g of reservoir crude oil is dissolved in 40ml n-hexane and is used in the determination of fractions. Figure 11 shows the HPLC equipment used for the separation of the fractions.

3.1.8 Ostwald Viscometer and Pycnometer

Viscometer is generally used to measure the viscosity of the solutions. This works based on the time taken by the fluid to pass through the specific points marked on the tube. The tube is thicker on one side and thinner on the other side Figure 12. On the bottom of the thinner tube there is a smaller diameter capillary that allows the fluids to pass through it. The fluid is then collected in a space between the two marks i.e. upper mark and lower mark. The fluid is sucked up to the upper mark and time is started once it reaches the exact place of upper mark. It is allowed to go down until it reaches the lower mark of the tube and the time is stopped. The time is noted and average is taken for at least three time measurements and then it is kept in the formula to calculate the dynamic viscosity of the fluid. It is given as:

$$\mu = Tavg * C * \rho \quad (4)$$

Where;

μ is the dynamic viscosity

Tavg is the average time taken by fluid to pass through marked points

C is the constant for viscometer used

ρ is the density of the sample.

Pycnometer is a small container used to measure the density of the solution having a specific volume. The fluid is poured in the pycnometer and the lid is inserted so that the excess amount of solution comes out of pycnometer. Then it weighted and the mass of the solution is find out. The volume of the pycnometer is already known so density can easily be calculated. Figure 13 below shows the schematic of pycnometer used.

3.1.9 Reverse Flow Viscometer

Reverse flow viscometer is used for the viscosity measurements of opaque liquids. Viscosity of heavy crude oil is measured using reverse flow viscometer at different temperatures. The tube is thicker on one side and thinner on the other sideError! Reference s ource not found.. The thinner tube is placed in the oil in inverted position and the suction is applied from the thicker tube and oil is filled in the ball of thinner tube. The viscometer is placed in constant temperature bath for viscosity measurements. The thinner tube opening is closed by a stopper to stop the flow of oil. After it attains the temperature for 30 minutes, the stopper is removed and the oil is allowed to flow in the lower bulbs. The time is measured for the flow and used in the equation (4) for kinematic viscosity measurement.

Figure 10: Multi position Stirrer

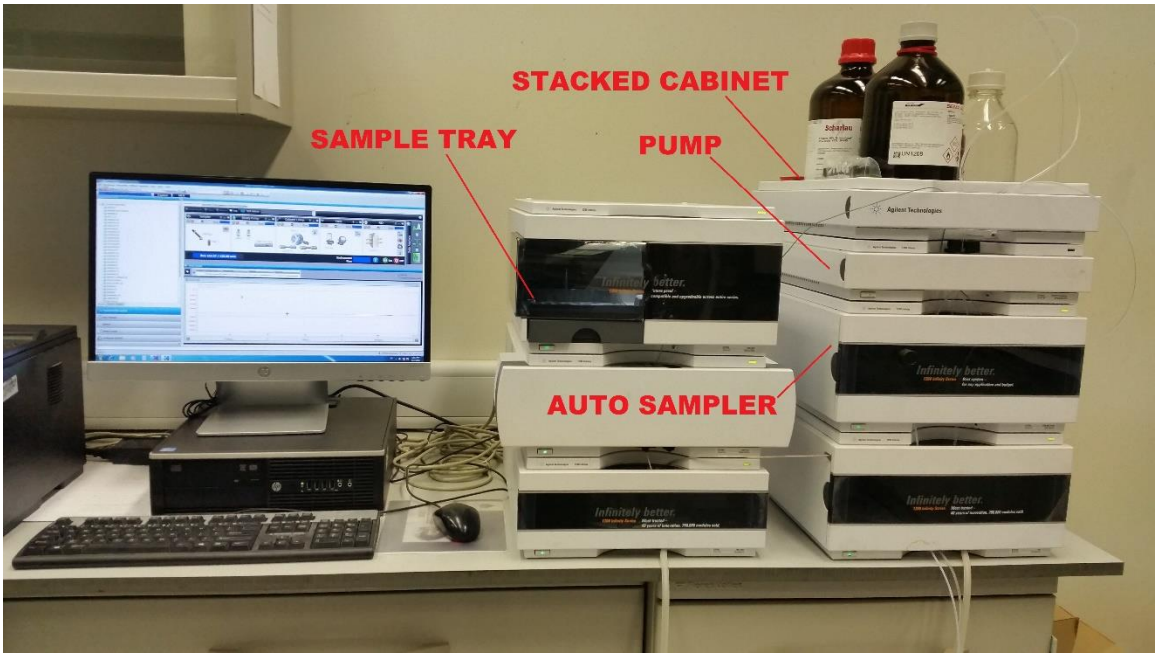

Figure 11: HPLC for SARA Analysis

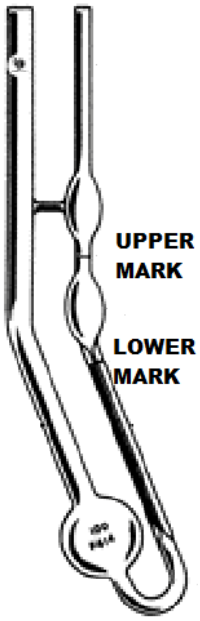

Figure 12: Ostwald Viscometer

Figure 13: Pycnometer

3.1.10 Spinning Drop Tensiometer

Spinning drop tensiometer is basically used for the measurement of interfacial tension between the high dense phase and low dense phase. The instrument used for the study is spinning drop tensiometer from Kruss Site 100 which is shown in Figure 14. The main term affected by the increase or decrease in the interfacial tension is the capillary number. The high dense and low dense phases are injected into the capillary tube Figure 15. The images of the drop phase are analysed with a camera installed within the equipment. This tool comes with a software and can measure the ultralow interfacial tension between the liquids. The temperature control unit maintains the desired temperature required inside the capillary tube. The two knobs on the instrument are used for adjusting the rotation speed of the capillary and the illumination such that the camera captures the movement of drop phase.

Measuring Principle:

When a heavy bulk phase and a light drop phase are situated in a horizontal, rotating capillary, the drop radius perpendicular to the axis of rotation depends on the interfacial tension γ between the phases, the angular frequency ω of the rotation and the density difference $\Delta\rho$. Drop diameter is determined by the video image of the drop by means of drop shape analysis. Thus, with a given speed of rotation and with known densities of the two phases, the interfacial tension can be calculated from the measured drop diameter d (=2r) in accordance with Bernhard Vonnegut equation (1942):

$$\sigma = \frac{r^3 * \omega^2 * (\rho_H - \rho_L)}{4} \quad (3)$$

Where

σ is the interfacial tension

r is the drop radius

ω is angular frequency of rotation

$\rho_H - \rho_L$ is the density difference between two phases

Spinning drop tensiometer measures ultralow interfacial tensions that are very useful in studying the behaviour between the solutions of high dense phase and low dense phase that are being used for enhanced oil recovery.

3.1.11 Thermo Gravimetric Analyzer (TGA)

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Measurements from thermogravimetric analysis are used primarily to determine the composition of materials and to predict their thermal stability. Thermogravimetric analyzer (TGA) SDT Q 600 unit of TA Instrument was used. Nitrogen was used as a carrier gas with a flow of 100 mL/min under a heating rate of 10^{o}C/min up to 600^{o}C.

TGA shown in Figure 16 consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. The plot of weight/mass against temperature or time produced by a thermogravimeter is called Thermogram.

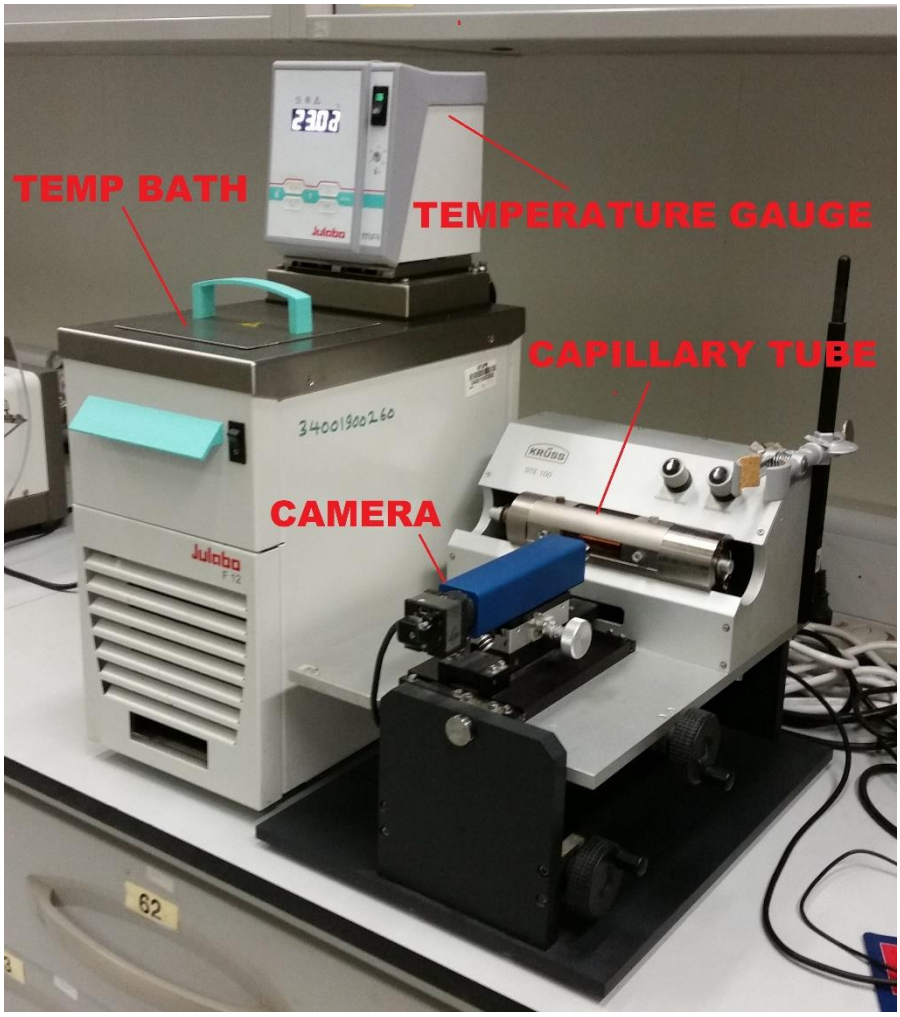

Figure 14: Spinning Drop Tensiometer

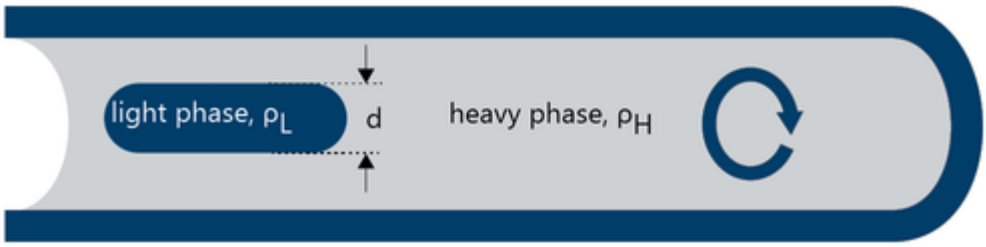

Figure 15: Schematic of Spinning Drop Method

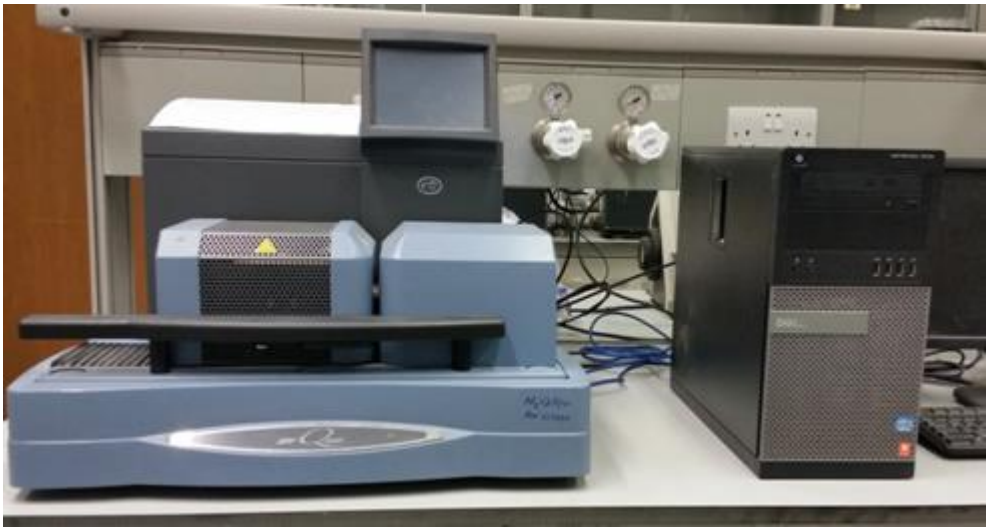

Figure 16: Thermogravimetric Analyzer

3.1.12 Long term Thermal Stability Setup

For the measurement of long term thermal stability of the Viscoelastic surfactant a setup is designed shown in Figure 17. The setup consists of electrical heaters, condensers, 500ml three way flasks, thermometers, glass connector, nitrogen cylinder, vacuum port, water supply and several connector pipes. Thermometer is installed from one neck of the flask to monitor the temperature inside the flask. The thermal stability is checked by purging the nitrogen and creating the conditions under nitrogen atmosphere. Vacuum is applied every time the sample is taken from the flask to avoid any oxidation of the solution. The other end of the flask is used for the sampling purpose. Continuous water is supplied to the condensers so that the vapours formed from the sample can be cooled down and the turned back to the flask and there is no loss in the solution.

3.1.13 Fourier Transform Infrared

Fourier Transform Infrared abbreviated as FTIR is a technique in which infrared radiations are passed through the sample and some radiations get absorbed and some radiations are transmitted. The resulting signal at the detector is a spectrum representing a molecular 'fingerprint' of the sample. FTIR generates spectra with patterns that provide structural insights. Samples collected from long term thermal stability setup on different days are diagnosed using FTIR. Sample solutions are dried and are used as solid in the FTIR. The spectrum produced by this technique can be used for analysis or quantify the material for any loss. Figure 18 represents the FTIR equipment used for the purpose.

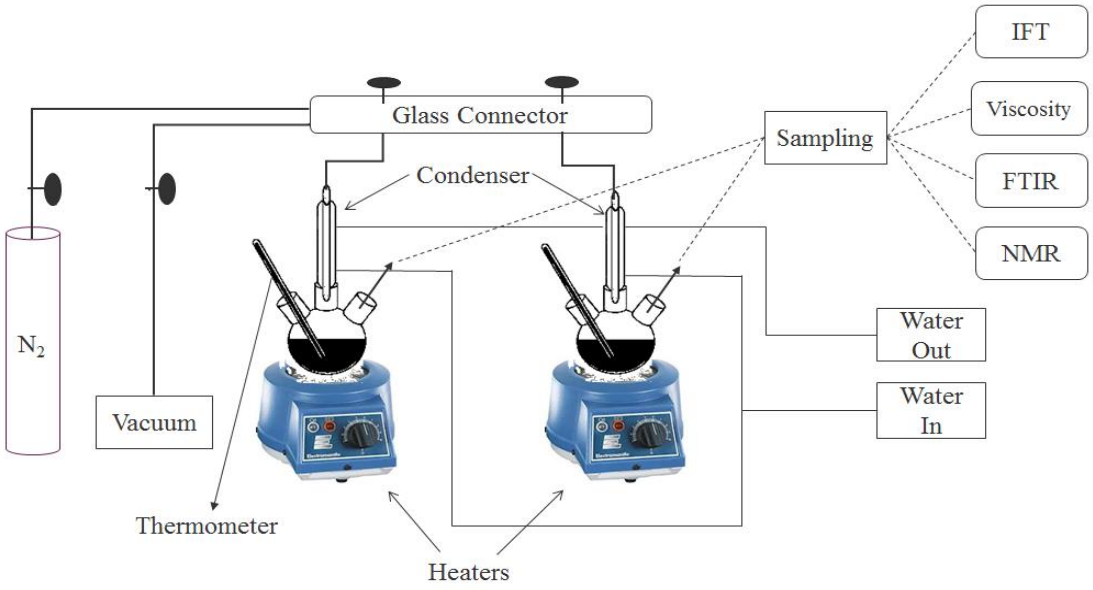

Figure 17: Long Term Thermal Stability Setup

3.1.14 Rheometer

Rheometer is an instrument by which rheological properties can be measured for the solutions. It can measure shear viscosity, elasticity and shear thinning etc. Figure 19 below shows the TA rheometer. Assembly for concentric cylinder is installed and used for the measurements. Solution required for the concentric cylinder is 25 ml. The system comes with a data acquisition software system that represents the measured data and the time required for the completion of the experiment. The key components of rheometer include the head assembly, rod, front panel, base, column, signal cable connection, coolant connections. Before using the equipment, it is make sure that the air supply and water supply to the machine is open. Sample is poured in the concentric cylinder assembly and the head is lowered so that it comes in contact with the top surface of the sample. The measurement modes can be selected from the software installed and the time and range for the measurements can be settled.

3.1.15 Shaking Water Bath

Shaking water bath represented in Error! Reference source not found. is an instrument that i s filled with heated water and can be used for shaking the samples at desired speed (rpm). The equipment has also the control for temperature. The temperature can be maintained while shaking the samples. It can be used at high temperatures for enabling any chemical reactions possible. There are separate control switches for shaking and temperature. It can also be used for providing continuous shaking and temperature at the same time for longer durations. The temperature sensing gauge that sense the temperature inside the shaking bath.

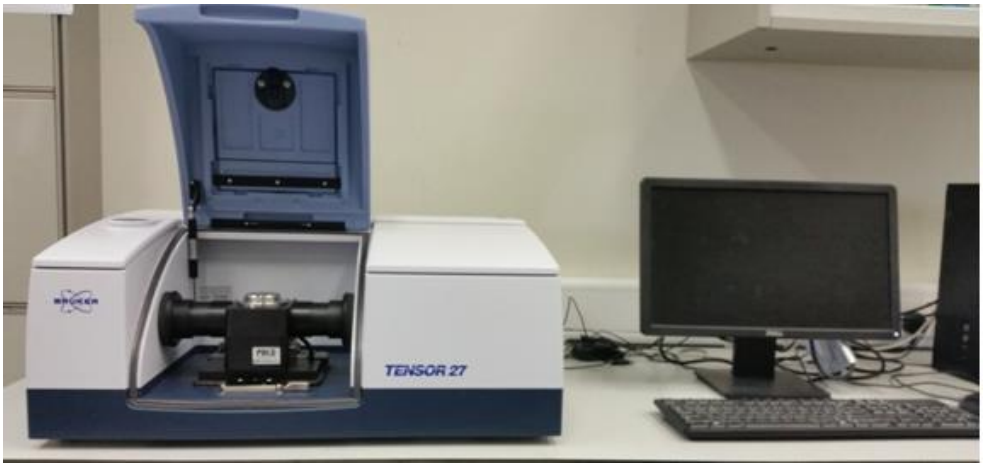

Figure 18: Fourier Transform Infrared

Figure 19: TA Rheometer

3.1.16 Zeta Potential

ZetaPALS zeta potential analyzer, manufactured by Brookhaven Instruments Cooperation shown in Figure 20 is used for zeta potential measurements. It consists of palladium electrodes that are mounted on the machine, a light source and a temperature sensor to measure the temperature near the sample. A data acquisition unit that measures the zeta potential. Electric field is generated when the light is passed through the sample. Light is scattered when the light strikes the moving particles in the cell. Zeta PALS utilizes light scattering to measure electrophoretic mobility of charged, colloidal suspensions. From the recorded shift of the phase, an electrophoretic mobility of particles will be measured which has a unit of (micron/second)/ (volt/cm). From measured electrophoretic mobility, the zeta potential will be calculated using Smoluchowski model for aqueous suspension or the Huckel model for particles suspended in solvents. Zeta potential is related to the charge of the interface surface between the rock and the concentration of the viscoelastic surfactant solutions used.

3.1.17 Core Flooding Apparatus

Core flood system from Vinci Technologies has been used for performing the core flooding experiments. Inside view of the equipment is shown in Figure 21. The instrument is equipped with core holder whose position can be adjusted, four hastelloy accumulators for the injection fluids. Back pressure valve is on the right side of the equipment. Several valves are located inside the oven that can be operated from the system.

Injection pumps are on the right side of the oven. Confining pressure can be applied from the pumps. A data acquisition unit that can monitor and display the inlet and outlet

pressures, flow rates and temperature inside the oven. Separator is located on the right side of the equipment to separate the phases from the effluent.

Core flooding setup usually consists of three main sections: the upstream section, core section and the downstream section. Upstream section includes pumps and accumulators for the injection of fluids in the cores. Core section includes the core holder and the sleeve, where cores are inserted, and confining pressure is applied. Downstream section covers the separator and the effluent collection stages. All systems are connected to a control and data acquisition unit for the monitoring and interpretation of data.

3.2 MATERIALS

The following chemicals, salts, oil and rock samples were used in the research study.

3.2.1 Brines

For the preparation of sea water and formation water different salts were utilized. Brines are prepared by the addition of specific weight of analytical grade salts in the deionized (DI) water. The composition used for the preparation of sea water and formation water is given in Table 1 and Table 2. Salts utilized for the preparation are:

- Na_2SO_4 – Sodium Sulphate
- $NaHCO_3$ – Sodium Hydrogen Carbonate
- NaCl – Sodium Chloride
- KCl – Potassium Chloride
- $SrCl_2$ – Strontium Chloride
- $CaCl_2$ – Calcium Chloride
- $MgCl_2$ – Magnesium Chloride

Figure 20: Zeta Potential Analyzer

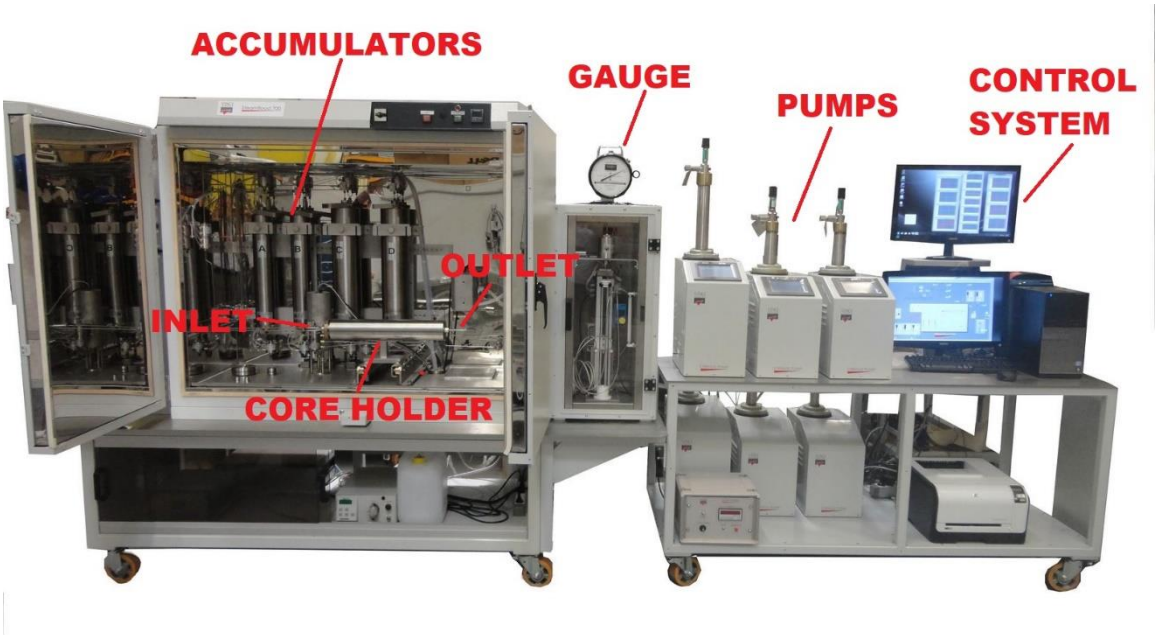

Figure 21: Core Flooding Apparatus

Table 1: Sea water composition

Ions	**Concentration (ppm)**
Na^{+}	18,300
Ca^{+2}	650
Mg^{+2}	2082.729
Cl^{-}	32200
HCO^{-3}	120
SO_4^{-2}	4290
Total	57,642

Table 2: Wafra formation water composition

Ions	**Concentration (ppm)**
Na^{+}	64,800
Ca^{+2}	13,710
Mg^{+2}	4721
K^{+}	2901
Sr^{+2}	609
Cl^{-}	146,800
HCO^{-3}	268
SO_4^{-2}	380
Total	234,189

3.2.2 Crude Oil

Crude oil from the Wafra Ratawi reservoir is used in the study. Crude oil is considered as heavy crude and the density of crude oil at different temperatures is measured and input in spinning drop tensiometer for the calculation of interfacial tension. Other properties of the crude oil are determined using HPLC for SARA Analysis. The properties of oil from SARA analysis are reported in the later section. Table 3 represents the properties of the crude oil.

Table 3: Properties of crude oil

Parameter	**Crude Oil**
API Gravity	17 ^{o}API
Density @ 30^{o}C	0.9393 g/cm^{3}
Density @ 50^{o}C	0.92507 g/cm^{3}
Density @ 80^{o}C	0.84596 g/cm^{3}

3.2.3 Core Samples

Carbonate core samples from the Wafra Ratawi reservoir are used for the experiments. The core samples are obtained from Chevron Saudi Arabia shown in Figure 22 . The porosity of the carbonate core samples lies in the range of 15% - 27%. Measured gas permeability lies in the range of 1 - 653 md. Core samples are mainly composed of calcite $CaCO_3$ as reported by the results of XRD.

Figure 22: Core Samples from Wafra Ratawi Reservoir

3.2.4 Deionized Water

Deionized water as the name suggest is a water that has the ions removed. Ions are either positively or negatively charged. For many applications, we require that these ions are removed from the water so that impurities in it may not react. It is used for preparation of brines and viscoelastic surfactant solutions. It is also used for cleaning purposes before and after each experiment to completely deionize and remove any impurities from mixing up.

3.2.5 Chelating Agent

Chelating agent (CA) is a chemical that controls the reactivity and properties of metal ions. DTPA (Diethylene Triammine Penta Acetic acid) is utilized in our research and its structure is given in Figure 23. DTPA is a polyamino carboxylic acid consisting of a diethylenetriamine backbone with five carboxylmethyl groups. Chelating agent has several functions in the reservoir. Chelating agents contain different functional groups (carboxyl, hydroxyl, ether, primary amine, tertiary amine, thiol, nitro, nitroso, and sulfine) that have the ability of seizing the multivalent cations (such as Ca^{+2}, Mg^{+2}, Al^{+3} and Fe^{+3}) to form a stable complex at a wide range of temperatures [85].

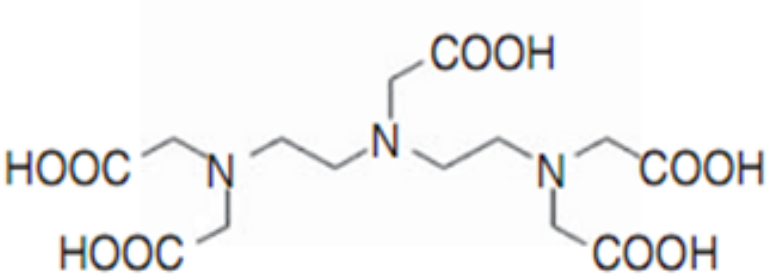

Figure 23: Structure of Diethylene Triammine Penta Acetic acid (DTPA)

3.3 Preparation of Solutions

3.3.1 Sea Water and Formation Water

Sea water was prepared by the dissolution of salts in deionized water as given in Table 1 section 3.2.1. and was used for the preparation of VES and VES/CA solutions of different concentrations. It is used as pre-flush and dissolving medium for chemicals in most of the EOR projects in high temperature and high saline reservoirs.

- Pour 1 liter of deionized water in a volumetric flask.
- Adjust salt concentrations (57,642 ppm) and add to deionized water according to the composition for sea water in Table 1.
- Use magnetic stirrer for stirring the solution.
- Stir the solution until all the salts get dissolved in deionized water.
- Filter the solution using standard filter paper and collect clear sea water.

Formation water was prepared by the addition of different salts in deionized water as presented in Table 2 section 3.2.1. Highly saline formation water of salinity 234,189 ppm was used in the core flooding phase where the cores were saturated with it and initial water saturation (S_{wi}) was calculated.

- Pour 1 liter of deionized water in a volumetric flask.
- Adjust salt concentrations (234,189 ppm) and add to deionized water according to the composition for formation water in Table 2.
- Use magnetic stirrer for stirring the solution.
- Stir the solution until all the salts get dissolved in deionized water.
- Filter the solution using filter paper and collect clear formation water.

3.3.2 Viscoelastic Surfactant Solutions

Viscoelastic surfactant solutions of different concentrations were prepared by the addition of VES in sea water of 57,642 ppm. Due to high salinity of the carbonate reservoirs sea water was used and preferred over fresh water.

Following steps are involved in the preparation of 0.5% of VES in 50 ml sea water.

- Clean the beaker with distilled water and dry.
- Use required volume from already prepared sea water.
- Add 30 ml of VES 1% and 50 ml of sea water to get 0.5% VES solution.
- Stir the solution using magnetic stirrer until clear solution is obtained.
- 2-3 days are required for viscoelastic surfactant solutions to dissolve properly.
- Once clear solution is obtained, keep the solution static for one day to let any bubbles settle down.
- For enhancing the growth of WLM and avoid foaming, slow speed is preferred while stirring.

Solutions preparation require proper stirring after the addition of VES in sea water to dissolve properly. Figure 24 below shows different concentration of VES in sea water solutions while stirring.

3.3.3 VES/Chelating Agent Solutions

VES/Chelating agent solutions were prepared by keeping the optimum VES concentration constant and changing the concentration of the Chelating Agent. High pH chelating agent DTPA was used for the preparation of solutions to avoid adsorption on the carbonate samples.

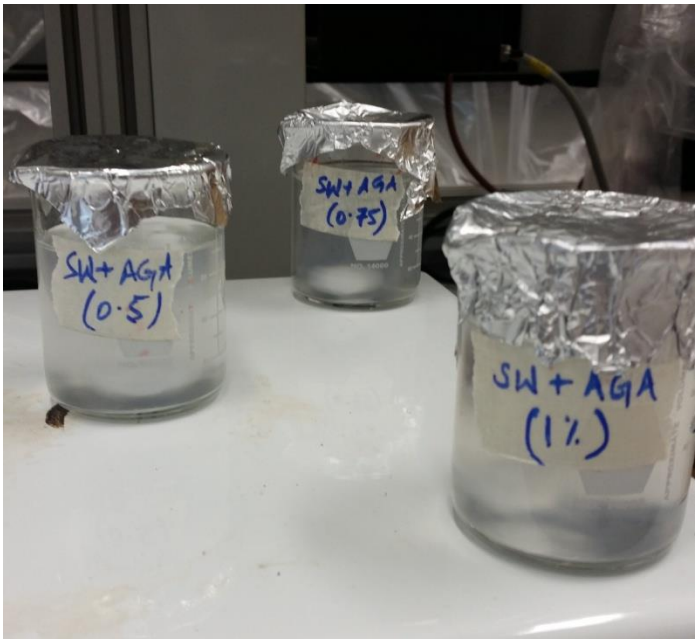

Figure 24: Stirring of VES in sea water solutions

Following steps are involved in the preparation of 0.3% VES–0.3% CA in 50 ml sea water.

- Clean the beaker with distilled water and dry.
- Use required volume from already prepared sea water.
- Add 15 ml of VES 1% and 35 ml of sea water to get 0.3% VES solution.
- Now by keeping 0.3% VES concentration constant, 0.3% chelating agent is added to get the final solution.
- Stir the solution using magnetic stirrer until clear solution is obtained.
- 1-2 days are required for VES/CA solutions to dissolve properly.
- Once clear solution is obtained, keep the solution static for one day to let any bubbles settle down.
- To avoid foaming of solution, slow speed is preferred while stirring.

3.4 Preparation for SARA Analysis

SARA analysis is performed to separate out Wafra Ratawi heavy oil sample into four chemical group classes, namely saturates, aromatics, resins, and asphaltenes, the so-called SARA fractions. Following steps were taken to perform SARA analysis:

- Take 40ml n-Hexane and approx.1g Wafra Ratawi crude oil in 60ml bottle and shake it so that all the oil is mixed with n-hexane.
- Keep it for 24 hrs so that all the oil gets mixed with n-hexane.
- Take 60cc syringe and 0.5 µm filter and weigh them both.
- Pour mixture of n-hexane and oil into the syringe while filter is attached.
- Filter the solution so that all the liquid part gets removed from the mixture.
- Remaining residual is asphaltene in syringe and filter.

- After all the liquid part is removed, rinse the solid asphaltenic part with fresh n-hexane and filter it in a separate beaker.
- Repeat last step to rinse.
- Now weigh the syringe and filter with asphaltenic content.
- Place the weighted syringe and filter in fume hood so that remaining liquid is removed from the solid parts.

3.5 High Performance Liquid Chromatography (HPLC) Procedure

HPLC equipment in Figure 11 was used for the separation of crude oil fractions. The sample prepared for SARA analysis was loaded in the machine and data acquisition system was used to start and end the experiment. Following steps were ensured to perform SARA analysis accurately:

- From 0-6 min collect eluting solution into the waste bottle.
- From 6-45 min collect aromatic solution into a marked beaker.
- From 45-120 min collect resin into another marked beaker.
- Evaporate the n-hexane from both beakers using rotary evaporator.
- Repeat all steps above as many times as possible until you get enough residue of both the aromatic and the resin.
- Weigh the residue of both beakers and record the values.

3.6 Density and Viscosity Measurements

Density measurements were performed using the density meter shown in Figure 12. Density measurements of aqueous solutions, viscoelastic surfactant solutions, oil and formation water were taken. Different temperatures were used for measuring the density

of samples. Working mechanism of density meter is described in section 3.1.7. Viscosity measurements of viscoelastic surfactant solutions and oil were performed using the ostwald viscometers, pycnometer and reverse flow viscometers. Working mechanism of both viscometers is described in 3.1.9 and 3.1.10.

3.7 Interfacial Tension Measurements

The SITE100 Kruss spinning drop tensiometer was used to determine the interfacial tension between the light phase (oil) and the heavy (VES solution) phase. The instrument and the measuring principle are described in section 3.1.8. This instrument is able to measure ultra-low interfacial tension values in the range of (10^{-4} – 10 mN/m). Both the heavy and the light phases are injected into a rotating capillary made of glass. The drop radius is perpendicular to the rotation axis and it depends on the IFT between the two phases (γ), the density difference between the heavy and light phases (ρ_H-ρ_L) and the rotation angular frequency (ω). According to Bernhard Vonnegut equation (1942), interfacial tension can be calculated using the following relation:

$$\gamma = \frac{1}{4}\left(\rho_H - \rho_L\right)\omega^2 R^3 \left(1 + \frac{2R}{3L}\right) \quad (5)$$

The lighter phase (oil phase) is injected into a rotating capillary that rotates with high speed and it is already filled with the heavy phase. The highspeed rotation of the capillary will cause the elongation of the light phase drop due to the centrifugal force on the drop. Interfacial tension will be equal to the centrifugal force. Parameters such as viscoelastic surfactant concentration, the addition of chelating agent and temperature was examined. The effect of chemical concentration for viscoelastic surfactant, chelating agent and temperature on interfacial tension is studied.

Steps involved in measuring the interfacial tension are:

- Firstly, sea water, VES and VES-chelating agent solutions are prepared.
- Different concentrations of all solutions are prepared for the measurement of IFT.
- Switch on the instrument starting with thermostat, then camera and then the software for the system.
- Adjust the temperature gauge to the desired temperature and apply.
- Remove the knobs on both sides of the capillary tube.
- Clean the capillary using a syringe with hot distilled water and if required with the cleaning brush.
- Inject hot distilled water from the right side of capillary and collect effluents from the left side of the instrument in the collecting flask.
- After cleaning the capillary tube, fill the glass syringe with heavy phase solution and inject in the capillary.
- Calibration is done by long needle to know the actual drop diameter.
- Densities of light and heavier phases are input in the software.
- Save the calibration reading and use it in measuring the IFT.
- Auto edge detection is selected from the software.
- Now close the inlet and outlet with knobs and adjust the rotation to low speed.
- Fill the other glass syringe having long needle with lighter phase i.e.oil and inject in capillary such that a drop is placed in the capillary.
- After that, increase the speed of the capillary and the oil drop will start to elongate.
- Adjust the camera position where it gives good resolution.
- Adjust the rotation speed such that oil drop gives cylindrical shape.

- Then the IFT is determined using the equation (5).
- Rotation speed is kept constant for long period of time so that the value of IFT stabilizes and it gives constant reading.
- Once stabilized value of IFT is obtained, it is saved in the computer.
- After completing the experiment, cleaning of capillary tube is required by removing the knobs on both sides.
- Again, hot distilled water is injected from right side to clean the capillary from inside and effluent is collected on the left side in collecting flask.
- It is recommended that if the temperature of system is high, it is cleaned at that temperature.
- After finishing the cleaning process bring the temperature back to room temperature conditions.
- Shut down the system in reverse order of software, computer, Instrument and then the thermostat.

Interfacial tension measurement in this research involved applicability of VES systems to Wafra-Ratawi reservoir conditions by determining the effect of chemical concentration and temperature on lowering the IFT. Here, both VES alone as well as VES/CA are used to explore the potential of in-situ generation of surfactants. Measurement of the interfacial tension (IFT) between the Wafra-Ratawi crude oil and the proposed VES systems is performed to screen the optimum concentration of VES sample in lowering the interfacial tension.

3.7.1 Effect of Concentration of VES on IFT

For the optimum VES concentration determination interfacial tension between filtered crude oil (light phase) and VES system (heavy phase) is evaluated. The concentration of VES system is varied from 0.1% to 1%. Salinity is kept constant and temperature is fixed for each concentration at 57,642 ppm and 50^{o}C. Time period used for the stabilization of IFT is 6,000 seconds. Procedure for the preparation of sea water and VES samples has already been discussed in the previous sections 4.1.1 and 4.1.3.

3.7.2 Effect of Temperature on IFT

Interfacial tension reduction depends on the temperature of the system. For this research three different temperature values are utilized to measure the IFT. The temperatures used are 30^{o}C, 50^{o}C and 80^{o}C. While the salinity and the concentration of the VES sample is kept constant at 57,642 ppm and 0.3%. Time period of 6,000 seconds is given for the stabilization of IFT value. The same temperatures are used for measuring the interfacial tension of VES and chelating agent with the crude oil.

3.7.3 Effect of VES with Chelating Agent on IFT

Chelating agent (DTPA) of high pH value is utilized with combination of sea water and VES to determine the interfacial tension of the solutions. Different concentrations of solutions are used to find the lowest IFT value. The procedure is same as described for the VES system but the only difference is the addition of chelating agent in the sea water and VES system. The concentration of chelating agent is varied from 0.1% to 1% while keeping the optimum VES concentration constant. Salinity is kept constant and temperature is fixed for each concentration at 57,642 ppm and 50^{o}C. Time period used for the stabilization of

IFT is 6,000 seconds. Procedure for the preparation of sea water, VES and VES/CA samples has already been discussed in the previous sections 4.1.1, 4.1.3 and 4.1.4.

3.7.4 Effect of Aging on IFT

Different tests of IFT were conducted to determine the optimum concentration. However, when it comes to high temperature reservoirs, EOR fluids need to sustain that high temperature for the effective results. For this, aging of VES sample of 0.3% concentration is evaluated at two different temperatures. The temperatures used for this purpose are 90^{o}C and 120^{o}C. Two experimental setups were installed to separately monitor the effect of aging on VES sample. Aging process continued for 30 days while the salinity, temperature and concentration of the system was kept constant for each experiment.

3.8 Thermal Stability

Two different experimental tests were performed to evaluate the thermal stability of the VES sample. These two tests include:

1. Thermogravimetric analysis (TGA).
2. Long term aging analysis.

3.8.1 TGA

Thermogravimetric analysis (TGA) is used to determine the composition of materials and to predict their thermal stability. TGA was performed using SDT Q600 (TA instruments) in nitrogen environment at a heating rate of 10^{o}C/min from 25^{o}C to 600^{o}C to evaluate the thermal degradation of VES.

Figure 18 shows the schematic of thermogravimetric analyzer. Thermal stability was evaluated through thermogravimetric methods. The temperature at which major change in

weight takes place was identified as the upper limit. VES and VES.CA samples were prepared with sea water as given in the section 4.1.3 and 4.1.4. Following steps were taken to perform the TGA analysis:

- VES and VES/CA samples were prepared with sea water.
- 10 ml of solution is taken and is dried.
- 30mg of dried sample is taken in Al_2O_3 crucible.
- Sample is placed in TGA holder.
- Nitrogen was purged at $20cm^3$/min.
- Sample in holder is heated at 5°C/min from 25°C to 600°C.
- Sample degradation was measured in terms of weight loss percent with an increasing temperature.
- Thermal stability of VES and VES/CA was tested.

3.8.2 Long Term Thermal Stability

The chemical thermal stability was studied in anaerobic environment using glove-box. The sample was prepared at 0.3% VES in sea water (57,642 ppm) and aged at two different high temperatures of 90°C and 120°C. Samples were taken at different time (for example, 1, 3, 10, 20 and 30 days) and run in FTIR, NMR, kinematic viscometer and IFT. Working principle and the schematic are described in section 3.1.12. Two experimental setups are prepared for each temperature condition. Nitrogen and vacuum are applied through the same glass connector having open/close valves. The FTIR analysis of viscoelastic surfactant samples was conducted. NMR sample was formed by transferring near about 100 mg of chemicals to 5 mm NMR tubes. NMR spectra was acquired using a JEOL 500 MHz spectrometer equipped with multi-nuclear probe. Kinematic viscometer was utilized

to measure the viscosity of the samples taken at different days. IFT for the aged sample at 30 days was measured using spinning drop tensiometer for both the temperature conditions of 90^{o}C and 120^{o}C. Following steps were adopted to perform long term thermal stability experiments:

- Setup was prepared by using electrical heaters, condensers, 500ml three-way flasks, thermometers, glass connector, nitrogen cylinder, vacuum port, water supply and several connector pipes.
- 0.3% VES was placed in 2 three-way flasks for two reservoir temperature conditions.
- Temperature knobs on the heating mantle were adjusted to 90^{o}C and 120^{o}C.
- Water was continuously supplied to condensers to avoid evaporation.
- Vacuum was applied every time the sample was removed from the bulk solution.
- Experiments were performed under nitrogen atmosphere in anaerobic environment.
- Thermometers were used on right side to monitor the temperature inside the three-way flasks.
- Sampling was done from the left side of three-way flasks.
- Long needle was used to extract the sample out using a 50cc syringe.
- Experiments were performed for 30 days to monitor the long term thermal stability.
- Samples were taken at 1, 3, 10, 20 and 30 days.
- Samples were used to perform FTIR, NMR, viscosity measurements and IFT.
- FTIR and NMR were used to detect structural changes in the VES.
- Results obtained were analyzed and reported.

3.9 Adsorption

Real core sample from Wafra Ratawi formation was used for adsorption studies. Static adsorption was conducted by adding viscoelastic surfactant concentrations to the crushed limestone core sample and analyzed for concentration analysis. The minimum conditioning time as well as the optimum solid/liquid ratio was determined. Following steps were undertaken to perform static adsorption:

- VES and VES/CA samples of different concentrations were prepared as described in section 4.1.3 and 4.1.4.
- Core samples were crushed by ROCKLAB crushing machine. No sleeves were used to avoid contamination.
- 2g of crushed-solid (limestone) was weighed and carefully transferred into 40ml glass screw-cap vials containing 30ml of viscoelastic surfactant solutions of known ionic concentrations.
- Teflon vials sealed and properly capped were used to avoid contamination and leakage especially at elevated temperatures.
- Teflon sealed screw-cap vials containing the samples were conditioned at the 30^{o}C and 60^{o}C temperature separately for 24 hours and left for at least another 24 hours at the same temperature without shaking to ensure that the samples have reached equilibrium.
- Conditioning of the samples at T°C was performed with shaking hot-water bath.
- Following equilibration, the supernatant viscoelastic surfactant solutions were carefully extracted with a 10ml syringe and filtered through a 0.45micron membrane syringe filter into properly labeled clean glass vials.

- The supernatant viscoelastic surfactant solutions, along with their initial concentrations were analyzed for ionic concentrations using TOC (Total Organic Carbon) equipment.
- Adsorption of viscoelastic surfactant solutions was measured at various concentrations using TOC.
- Static adsorption as function of VES and VES/CA concentration and temperature was analyzed.
- Results obtained were analyzed and reported.
- Dynamic adsorption was measured in reservoir conditions through core-flooding experiments.

The adsorption characteristics of VES and VES/CA systems on the reservoir rock were investigated. Effects of concentration and temperature were analyzed.

3.10 Zeta Potential Measurements

For suitable selection of VES and VES/CA concentration and stability, measurement of zeta potential in a formulation can be utilized to make valid choices about the chemistry of the formulation. Measurement of zeta potential helps in determining the effect of formulation on other bulk properties such as viscosity. The choices of VES and VES/CA used in the formulation has an impact on cost. Therefore, adjusting the dose of VES or VES/CA is of high importance.

ZetaPALS zeta potential analyzer, manufactured by Brookhaven Instruments Cooperation was used for zeta potential measurements. It calculates zeta potential of suspended particles in electrolyte solutions using Phase Analysis Light Scattering (PALS). Zeta potential

measurements were used to examine the influence of salts on micelles and help in identifying the conditions that lead to coalescence and aggregation. Such results helped us in explaining the findings from adsorption experiments by revealing the salt-VES and salt-VES/CA interactions. Knowledge of Zeta potential of VES micelles in a formulation were used to select the most appropriate VES and VES/CA concentration to provide stability. Following steps were performed to measure the zeta potential of the viscoelastic surfactant solutions.

- VES and VES/CA solutions of different concentrations were prepared as described in the previous sections 4.1.3 and 4.1.4.
- Core samples were crushed by ROCKLAB crushing machine. No sleeves were used to avoid contamination.
- 2g of crushed-solid (limestone) was weighed and carefully transferred into 40ml glass screw-cap vials containing 30ml of viscoelastic surfactant solutions of known ionic concentrations.
- Teflon vials sealed and properly capped were used to avoid contamination and leakage especially at elevated temperatures.
- The teflon sealed screw-cap vials containing the samples were conditioned at the 60^{o}C temperature for 24 hours and left for at least another 24 hours at the same temperature without shaking to ensure that the samples have reached equilibrium.
- Conditioning of the samples at T°C was performed with shaking hot-water bath.
- After the samples attain equilibrium state, electric conductance was measured using zeta potential analyzer.

- Zeta potential measurements on limestone suspension were performed at each 100 cycles.
- Auto mode voltage and 20 Hz frequency was specified to avoid contamination of sample from palladium electrodes.
- After each 5 cycles the run was stopped and the sample was checked for any contamination.
- Zeta potential was calculated using Smoluchowski model for aqueous suspension or the Huckel model for particles suspended in solvents. (Brookhaven Instruments Manual, 2002).

During the run, all reported data on the screen was monitored, especially, the value and the sign of displayed mobility in addition to the relative residual and phase shape. This process was repeated at least four times, while cleaning and conditioning the electrodes after each two runs until a good mobility was observed. This good mobility is defined as the average mobility from a range that has very close and stable values, stable sign and has good phase shape. To condition the electrodes, zeta potential measurement on pure original brine (with no particles) was conducted using 10 continuous runs, each one consists of 15 cycles.

3.11 Core Flooding

Core flooding is a laboratory experimental process where consolidated cores mostly sandstone and carbonate, replicative of porous natural reservoir, are flooded with an injection fluid to determine the efficiency of the injection fluids to recover oil and reduce the residual oil saturation. Schematic and working principle is described in section 3.1.17. Core flooding is used to evaluate the performance of water flooding and EOR. Firstly, water flooding is done to recover oil from the cores but after water flooding still some oil

is left in the cores. So, EOR is applied after water flooding to recover the residual oil present in the cores. Two core flooding experiments were performed in this research using sea water, VES and VES/CA of the optimum concentrations. Oil recovery experiments with core-flooding was carried out using core-samples from Wafra-Ratawi Reservoir. The composite core-samples were used. Core flooding equipment from VINCI Technologies was used for core flood experiments. Figure 24 shows detailed schematic of the core flood system. The following procedure was followed:

3.11.1 Core Preparation

Carbonate Cores of Wafra Ratawi formation were acquired as shown in Figure 25. Samples for core flooding were selected based on the porosity and permeability data and the shape of the cores. Cores of diameter 1.5" were used. Cores selected were cleaned properly for any contamination inside the cores using methanol and toluene. Cores were put into core cleaner where toluene was heated at about 80^{o}C. Toluene was evaporated and flowed through the core removing the fluid inside and then it condensates continuously in closed core cleaner. The cleaning process lasts one day. After that, the cores were dried at about 80^{o}C for another day. The dry weight of the cores was taken. The cores were vacuumed for about four hours to remove air inside the cores.

3.11.2 Pore Volume Measurements

The cores were saturated in the saturator with formation water (234,189 ppm) under confining pressure of 1500 psi for one day. Then, the cores were taken out and their wet weights were measured. After that samples were kept immersed in formation water for another two days for ions equilibrium with the core samples at room temperature. The pore volume (PV) was calculated based on the dry and wet weights of the core samples.

$$Pore\ Volume\ (PV) = \frac{Wet\ Weight - Dry\ Weight}{Density\ of\ Formation\ Water} \quad (6)$$

Density of the formation water was assumed to be 1g/cc at room temperature. So the PV is the difference in the wet and dry weights of the core samples.

3.11.3 Core Holder and Accumulators Setup

After saturating the core samples with formation water, the cores were loaded in the rubber sleeve of the core holder and spacers were placed. The accumulators were filled with formation brine, filtered crude oil, sea water and chemical solutions of VES and VES/CA. Confining pressure replicative of overburden pressure in the reservoir of 500 psi was applied to check any leaks in the core holder. Once ensure that no leaks in the system, all the lines were connected and back pressure of 1000 psi was applied. Confining pressure was increased to 2000 psi once injection of formation water started. Both the upstream and the downstream was purged with formation water to remove air in the piping system.

3.11.4 Permeability and Initial Water Saturation

Formation brine (234,189 ppm) was injected through the core samples at flow rate of 0.25 ml/min initially to equilibrate the pressures and temperature of the system. Permeability is basically the ability of porous medium to allow the fluids to pass through it. Brine permeability was measured by injecting formation brine at different flow rates (q) and noting the corresponding pressure drops (ΔP). Permeability measurements were started by flowing the formation water through the core until pressure difference is stabilized. The flow rate was increased to 0.5 ml/min until pressure stabilized. The same procedure will be done with flow rates of 0.75 ml/min and 1 ml/min. The flow rate versus pressure drop was plotted and the slope (m) was determined. Having the slope, values were substituted

in the Darcy law to measure the permeability (K). Once the permeability value was determined, the flow was changed from formation brine to filtered crude oil. Oil was injected in the cores at 0.5 ml/min to displace the formation brine and measure the initial water saturation (S_{wi}). Oil was injected for almost 2 PV until no more water was coming out and the effluents were collected in the 50 ml cylindrical flasks to measure the amount of water recovered. Temperature of the system was maintained at 90^{o}C.

3.11.5 Aging Cores with Oil

The next stage followed by permeability measurement and initial water saturation is aging the core samples with oil. Once the samples were fully saturated with oil under confining pressure and back pressure, the core samples were left under 90^{o}C for aging process. Aging lasted for 15 days. Temperature and the pressures were maintained during the whole period.

3.11.6 Water flooding

After aging the core samples for 15 days, oil recovery process was started by flooding sea water brine with salinity concentration of 57,642 ppm at flow rate 0.5 ml/min. Confining pressure of 2000 psi and back pressure of 1000 psi were maintained. Oil was displaced with sea water brine until no more oil was produced at the end collection point. Pressure drop was continuously monitored during the whole experiment. The effluents were collected in 15 ml graduated tubes for each pore PV. Oil recovery was noted and pressure drop profile was monitored. Remaining oil saturation and the corresponding PV's were determined.

3.11.7 VES and VES/CA flooding

Chemical flooding was started by injecting slug solution through the core samples, and oil recovery percent and pore volume injected were calculated. The chemical solutions of optimum concentration 0.3% VES and 0.3% VES–0.3% CA with 57,642 ppm brine was used. Slugs were injected in both experiments at flow rate of 0.5 ml/min. The optimum chemical concentration from IFT, thermal stability, adsorption and zeta potential was considered for injection. VES and VES/CA injection in both experiments continues until there was no oil coming out at the end collection point. The effluents were collected in 15 ml graduated tubes for each pore PV. Oil recovery was noted and pressure drop profile was monitored. Remaining oil saturation and the corresponding PV's were determined.

3.11.8 Water flooding

Having flooded the core samples with VES or VES/CA solutions, again sea water brine with salinity concentration of 57,642 ppm was injected at flow rate of 0.5 ml/min to remove any additional oil that can be recovered. The effluents were collected in 15 ml graduated tubes for each pore PV. Remaining oil saturation and the corresponding PV's were determined.

In this phase of experiments, the optimum VES and CA/VES systems that pass the IFT, thermal stability, adsorption and as well as compatibility tests were subjected to performance evaluation in core-flooding. Crude oil sample from Wafra-Ratawi reservoir was used. Guided by the results of previous experiments, selected core-flood displacement tests were performed to confirm the results and optimize the EOR process. The two potential systems VES and VES/CA were screened under typical reservoir conditions through core-flooding experiments.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Porosity and Permeability

Porosities and permeabilities of the core samples used were measured using helium porosimeter described in section 3.1.1 and the PV's were calculated using the equation 6. Below are the tables that calculates the PV for the core samples used for two experiments of core flooding. Table 4 calculates PV of core samples 4A, 52 and 54 obtained from Well R-118 and their total PV is 38.668 cm^3. Range of porosity values lies within 19-24 % and the permeability values range for these samples is approx. from 91-210 md. In Table 5 PV of cores 3, 64 and 69 obtained from Well R-146 are calculated and their total PV is 38.31 cm^3. Range of porosity values lies within 22-25 % and the permeability values range for these samples is approx. from 215-403 md.

4.2 Thin Section Analysis

Four thin sections were prepared from the cores 14 and 79V of Wafra Ratawi formation obtained. The top and bottom sections were sliced from these cores and used for the preparation of thin section slides. In the following, the detailed petrographic studies of these samples are presented which consist of primary carbonate particles, the depositional and digenetic fabrics, and porosity types. It can be noted in that brownish color represents the grain particles whereas the bluish green color represents the porous region.

Table 4: Rock properties of core samples 4A, 52, 54

Cores	Porosity	Permeability	Length	Diameter	Dry Weight	Wet Weight	Pore Vol.
	(%)	(mD)	(cm)	(cm)	(gm)	(gm)	(cm^3)
4A	19.033	176.19	4.266	3.787	103.8	114.424	10.624
52	23.36	210.69	4.547	3.749	101.502	115.099	13.597
54	23.88	91.26	4.688	3.742	103.78	118.227	14.447

Table 5: Rock properties of core samples 3, 64, 69

Cores	Porosity	Permeability	Length	Diameter	Dry Weight	Wet Weight	Pore Vol.
	(%)	(mD)	(cm)	(cm)	(gm)	(gm)	(cm^3)
3	22.017	339.6	4.484	3.776	105.485	118.175	12.69
64	26.51	215.68	3.937	3.749	92.296	103.771	11.475
69	24.92	403.06	4.305	3.742	97.426	111.571	14.145

Sample from Top of Core 14

Figure 25 shows the thin section prepared from top slice of core sample 14 that can be described as uniform distribution with fine grains. Main composition of the rock is peloids with some bioclasts such as echinoids, forams and bivalves. Grains are squeezed that shows evidence of compaction on the rock fabric. The porosity shown in the bluish green color is mainly intraparticle. Moldic porosity is also present. Rock fabric is packstone to mudleane packstone.

Sample from Bottom of Core 14

Figure 26 shows the thin section prepared from bottom slice of core sample 14 that can be described as heterogeneous with fine grains and coarse grains. Some micrite is also present between the grains. But it is mainly composed of peloids with some bioclasts such as echinoids, forams and bivalves. The porosity shown in the bluish green colour is mainly intraparticle with some moldic and some intra skeletal porosity. Rock fabric is packstone to mudlean packstone. The particles are mostly micritized. Some of the grains are squeezed that is the evidence of compaction on the rock fabric.

Sample from Top of Core 79V

Figure 27 shows the thin section prepared from top slice of core sample 79V that can be described as grainstone with fine and coarse grains. Majority of the grains present are peloids. Some echinoids and some forams are also present. Grains are micritized. Big bivalve is present between the grains. The porosity shown in the bluish green colour is mainly intraparticle with some intra skeletal porosity. Rock fabric is mudleane packstone. Grains are squeezed and not visible due to the compaction.

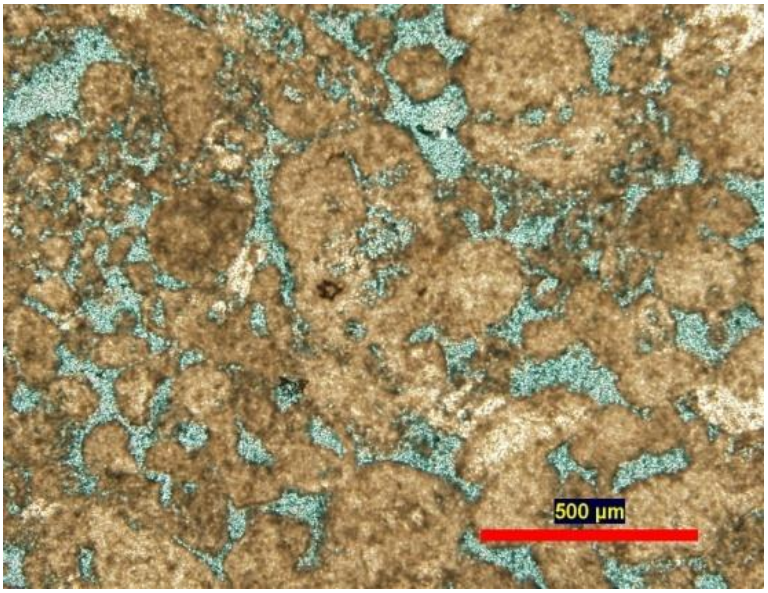

Figure 25: Thin section image of core sample 14 top

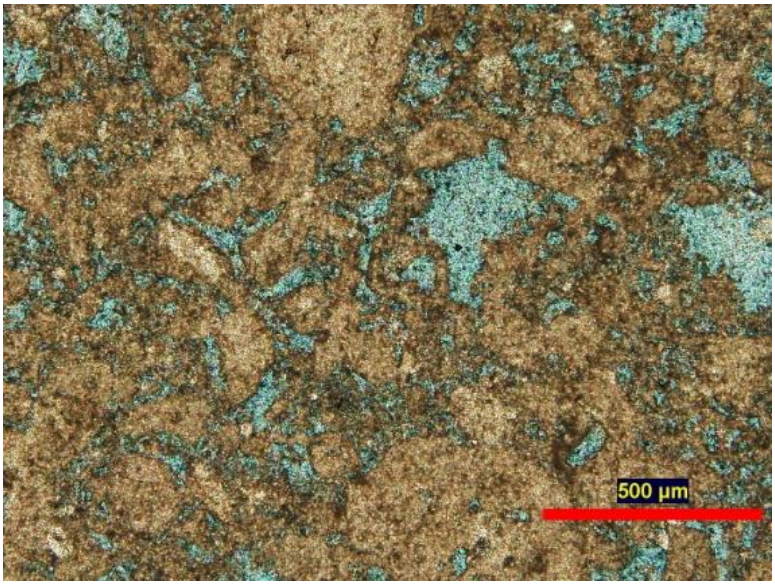

Figure 26: Thin section image of core sample 14 bottom

Sample from Bottom of Core 79V

Figure 28 shows the thin section prepared from bottom slice of core sample 79V that can be described as homogeneous with fine and coarse grains. Some micrite is also present between the grains. But it is mainly composed of peloids with some bioclasts such as echinoids, forams and bivalves. The porosity shown in the bluish green colour is mainly intraparticle with some moldic and some intra skeletal porosity. Rock fabric is packstone. Some bivalve grains are also present. Some of the grains are squeezed that is the evidence of compaction on the rock fabric.

4.3 X-ray Diffraction and X-ray Fluorescence

XRD and XRF is an analytical technique for the identification and quantitative determination of crystalline compounds. Calcium carbonate samples were crushed into fine powder for characterization. Structure and composition of calcite samples powder was determined using X-ray Diffraction and X-Ray Fluorescence. The diffraction pattern was collected at a scanning rate of 0.02 degrees per second in 2θ ranging from 0° to 80° using X-ray diffractometer described in section 3.1.2. The 2θ peak positions can be used as a fingerprint to identify crystal phases. $CaCO_3$ phase can easily be distinguished by XRD in Figure 29. For the quantitative analysis XRF is performed to get the concentration of each element present in the powdered sample. Table 6 presents the data obtained with XRF. Samples are rich in Ca crystalline minerals and the major phase is calcite while some impurities are also present like Aluminum (Al), Phosphorus (P), Silicon (Si) and some traces of Iron (Fe).

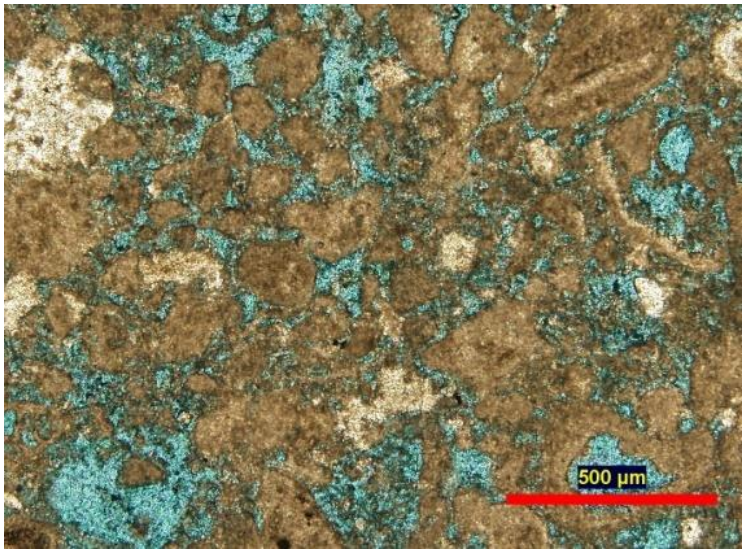

Figure 27: Thin section image of core sample 79V top

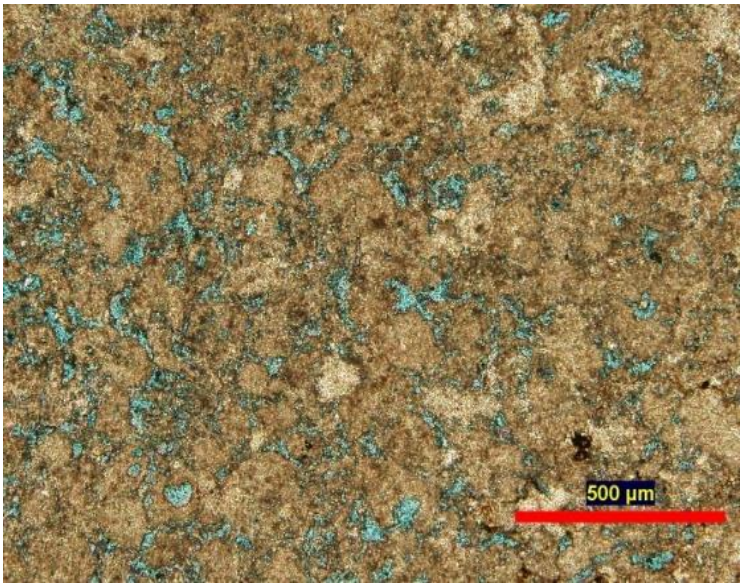

Figure 28: Thin section image of core sample 79V bottom

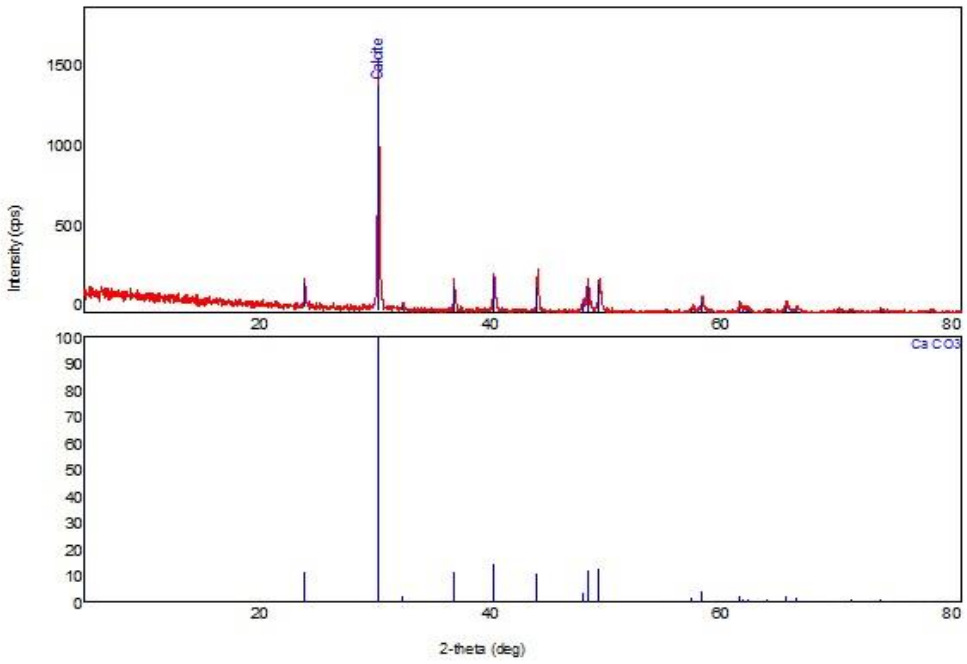

Figure 29: X-Ray Diffraction Analysis

Table 6: XRF Analysis

Element	**Symbol**	**Concentration (%)**
Calcium	Ca	97.885
Aluminum	Al	0.880
Phosphorus	P	0.705
Silicon	Si	0.326
Iron	Fe	0.202

4.4 SARA Analysis

Composition of crude oil has a huge impact on the effectiveness of some enhanced oil recovery techniques. The analysis that is used for separating the hydrocarbon sample into different fractions commonly saturates, asphaltenes, resins and aromatics (SARA). HPLC technique was used to perform SARA analysis of heavy crude oil of 17^{o} API. The saturate fraction consists of nonpolar material including linear, branched, and cyclic saturated hydrocarbons. Aromatics, which contain one or more aromatic rings, are more polarizable. The remaining two fractions, resins and asphaltenes, have polar substituents. The distinction between the two is that asphaltenes are insoluble in an excess of heptane (or pentane) whereas resins are miscible with heptane (or pentane). This classification system is useful because it identifies the fractions of the oil that pertain to asphaltene stability and thus should be useful in identifying oils with the potential for asphaltene problems. The detailed procedure for SARA analysis and HPLC is described in sections 4.1.5 and 4.2 respectively. The SARA fractions measured by HPLC technique are summarized in Figure 30 and Table 7.

4.5 Density Measurements

Densities of the following solutions were determined for use in the interfacial tension measurements:

1. Sea Water with VES-AGA-97
2. Sea Water with VES- AGA and CA
3. Crude oil

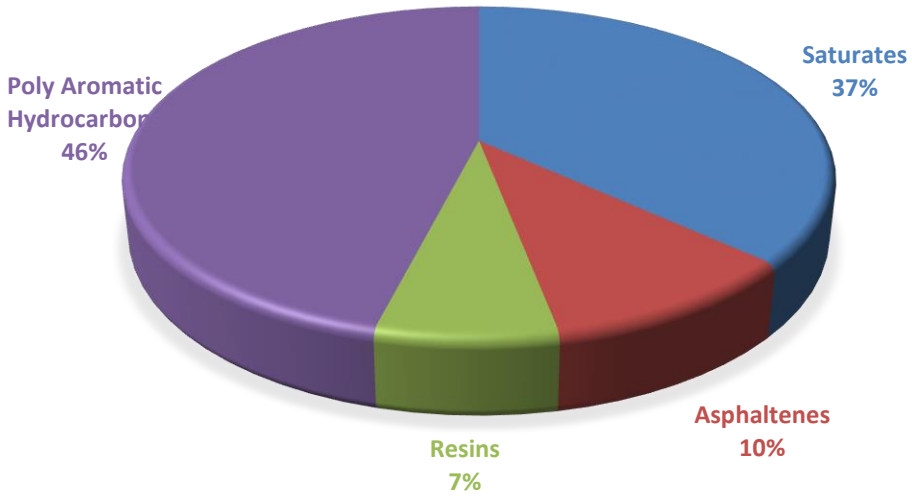

Figure 30: Compositional analysis of crude oil

Table 7: SARA analysis of crude oil

Components	**Composition %**
Saturates	36.77
Asphaltenes	10.2
Resins	7.01
Poly Aromatic Hydrocarbons	46.02
Total	100

It can be seen from the Figure 31 through Figure 33 that density is affected by the temperature change. Table 13 through Table 15 gives values for density measurements. With the increase in temperature, the density of VES solutions decreases because as temperature increases, kinetic energy of the particles also increases that cause the particles to move faster and hence density of the solutions decrease.

4.6 Viscosity Measurements

Viscosity is the measurement of the resistance to flow. Viscosifying ability of the VES solutions and oil were determined using kinematic viscometer, reverse flow viscometer and rheometer. Figure 34 shows the trend of crude oil viscosity with the increase in temperature. Table 11 and Table 12 gives viscosity values for oil and VES respectively. Measurements were taken at four different temperatures of 30^o, 50^o, 70^o and 90^oC. Increase in temperature usually causes the thermal or kinetic energy of the molecules to increase, and hence the viscosity decreases. Also, the cohesive forces are reduced with an increase in temperature and the intermolecular forces increases. Figure 35 gives the plot of concentration of viscoelastic surfactant solutions on x-axis while the viscosity of the solutions on y-axis. The measurements are taken at constant shear rate of $5s^{-}1$. By increasing the concentration of VES in sea water, viscosity also increases. Depending upon the concentration, more VES in sea water means more viscous solution.

4.7 IFT Characterization

The most important parameter for the selection of any EOR technique is the reduction of interfacial tension between the fluid injected and the oil present in the reservoir. Spinning drop tensiometer was used to determine the IFT between the VES solutions and the crude oil described in section 3.1.8. In this section, the results of IFT are discussed. Effect of

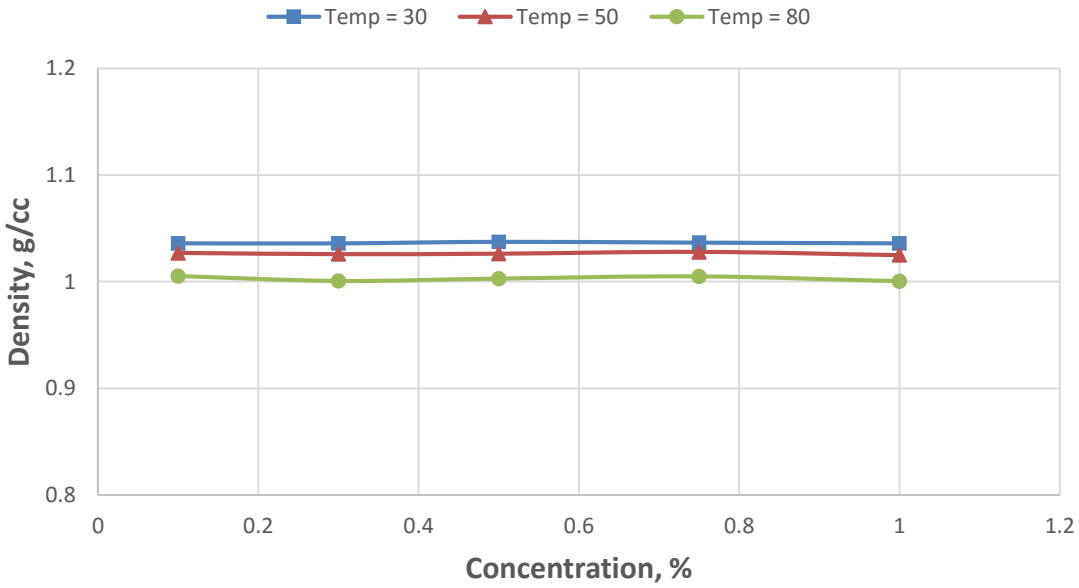

Figure 31: Effect of temperature on density of VES AGA

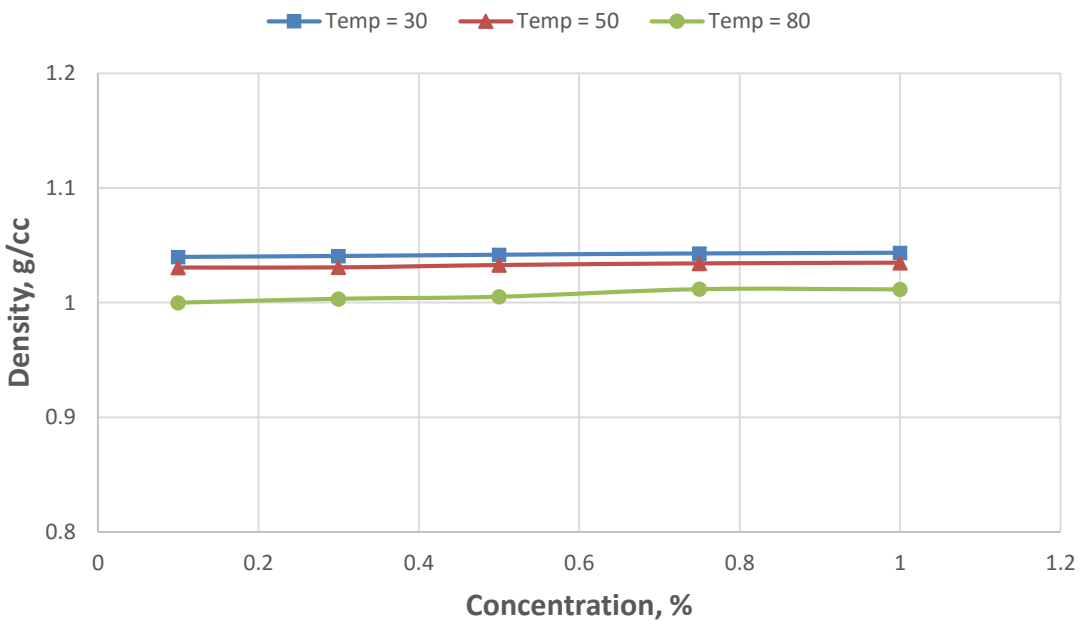

Figure 32: Effect of temperature on density of VES AGA with CA

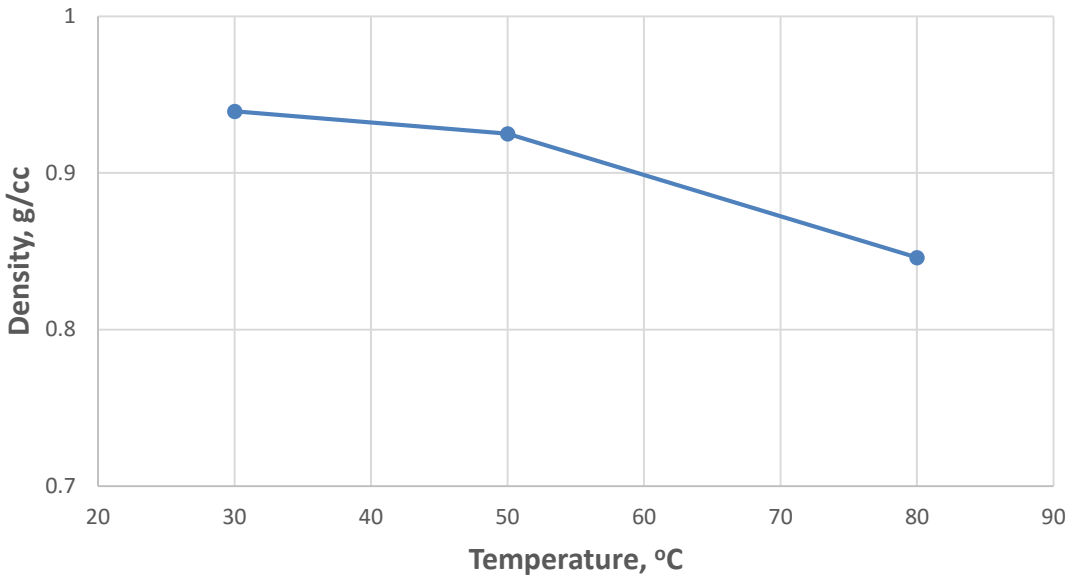

Figure 33: Effect of temperature on density of crude Oil

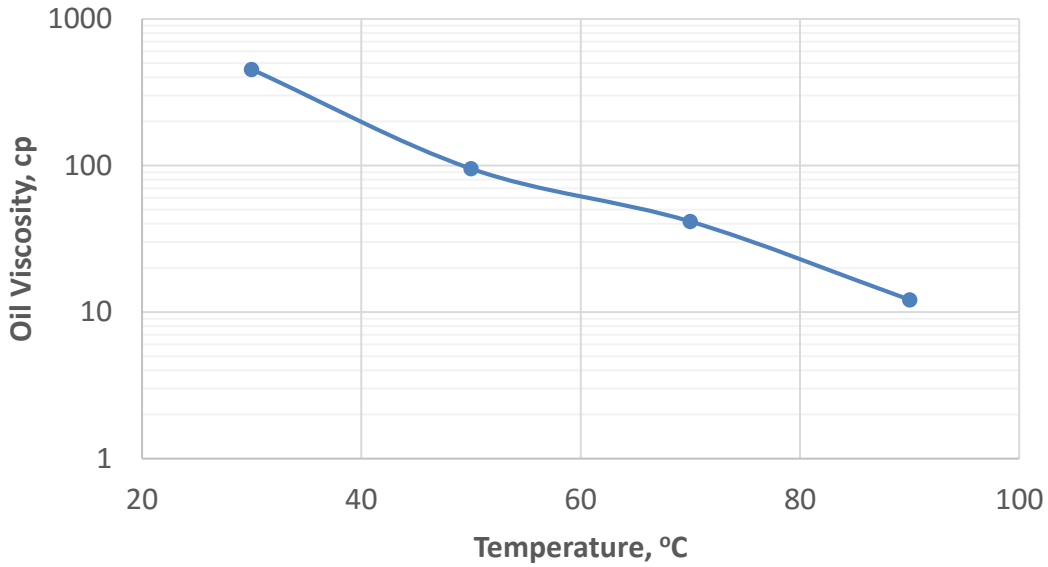

Figure 34: Effect of temperature on crude oil viscosity

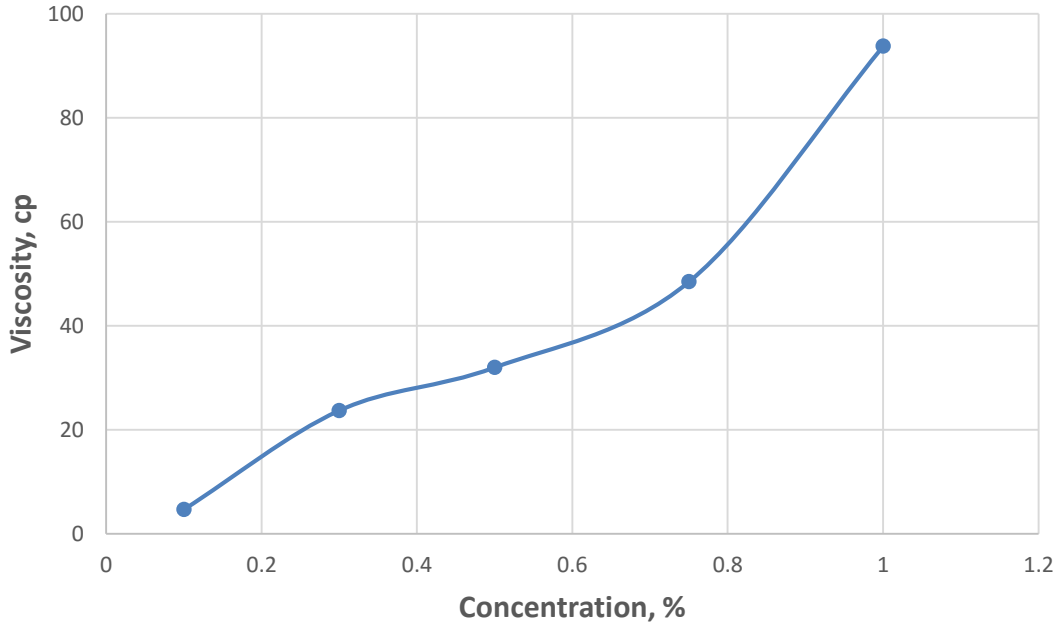

Figure 35: Viscosity of VES prepared in sea water at 30°C

various parameters like concentration, temperature, time and addition of chelating agent are investigated. Comparison of VES and VES-CA is performed on IFT reduction with temperature and time. Also, the viscosity/IFT ratio is determined to select the best optimum VES concentration to be used.

4.7.1 Effect of Concentration

Interfacial tension between VES solutions of different concentrations and crude oil is presented in Figure 36. VES solutions were prepared of concentrations from 0.1-1% with sea water of salinity 57,642 ppm and their IFT was determined. The test was performed at 50^{o}C and time allotted was 6000 seconds for the IFT to get stable. It can be seen that IFT is decreasing with the increase in concentration of VES. But the decrease is not much after 0.3% of concentration and it stabilized after 0.75%. IFT is very sensitive to concentration, temperature and salinity [86]. Interfacial tension between VES solutions with addition of chelating agent is presented in Figure 37. Solutions were prepared by keeping the VES concentration constant of 0.3% and changing the concentration of chelating agent from 0.1-1% with sea water of salinity 57,642 ppm and their IFT was determined. The same temperature and time conditions were applied as for the VES solutions without chelating agent. IFT reduction is a phenomenon where there could be non-linearity [6]. It can be observed from the Figure 40 that IFT is behaving nonlinear. It decreases at first and then increases from 0.3 – 0.75%. From 0.75% till 1% it again shows decreasing trend. Micelles formation in VES and the combination of VES-CA solutions are very sensitive to concentrations of the chelating agent. There exists the non-linearity with IFT reduction through surfactants [87].

4.7.2 Effect of Temperature

Temperature has great impact on the IFT response. Many studies have been presented in the past for the measurement of IFT between crude oil and brine at reservoir temperatures and pressures [88]. Figure 38 shows the effect of temperature on IFT when 0.5% VES solution was used with sea water of salinity 57,642 ppm. The time allotted for each measurement was 6000 seconds. It is clear from the graph that lowest IFT is measured at 50^{o}C. IFT decreases from 30^{o}C until 50^{o}C and then increases at 80^{o}C. IFT is very sensitive to concentration, temperature and salinity [86]. IFT behavior depends mainly on the composition of oil, brine and VES solution concentrations used. Decreasing trend of IFT could be due to the weakening of intermolecular forces at the oil/VES interface. While increasing trend of IFT at high temperatures could be due to inverse temperature effect on the solubility of surfactants [89]. Solubility may also decrease with the increase in temperature. Micellization is affected by various factors including surfactant nature (chain length, hydrophobic volume, and head group area), temperature, solvent, additive, pressure, pH, ionic strength, etc. [90] For viscoelastic surfactants, micellization is affected by temperature as the hydrophobic and head group interactions change with temperature. This is due to an increase in the destruction of hydrogen bonds between water molecules and surfactants hydrophilic groups. Further for VES, the complexity comes in terms of interfacial viscosity [6] and short thermoviscosfying nature. Increase in interfacial viscosity leads to increased non-Newtonian behavior or rigid behavior at the interface leading to the unfavorable consequences in the displacement efficiency or IFT reduction [6]. Figure 39 shows the effect of temperature on IFT when 0.3% VES 0.3% CA solution

was used with sea water of salinity 57,642 ppm. The same trend is obtained as for VES solution.

4.7.3 Effect of Adding Chelating Agent

In the previous sections, effect of concentration of VES solutions and temperature has been discussed. Chelating agent (DTPA) of high pH of 12 is used in this research. Addition of chelating agent is done in order to suppress the cations present in the reservoir that cause the sorption of crude oil. Figure 40 shows the effect of addition of chelating agent in the VES solutions. VES-CA solutions were prepared of concentrations from 0.1% - 1% with sea water of salinity 57,642 ppm and their IFT was determined. The test was performed with 0.3% VES and 0.3% VES, 0.3% CA. The time allotted was 6000 seconds for the IFT to get stable. It is clear from the graph that lowest IFT is measured at 50^{o}C for both cases. IFT decreases from 30^{o}C until 50^{o}C and then increases at 80^{o}C. IFT is very sensitive to concentration, temperature and salinity [86]. IFT behavior depends mainly on the composition of oil, brine and VES solution concentrations used. Higher IFT is attained with VES-CA solutions at 30^{o}C and 80^{o}C rather than VES solutions. But the lowest IFT is attained by both systems at 50^{o}C and of approximately same value. IFT reduction is a phenomenon where there could be non-linearity [6]. It can be observed from the Figure 40 that IFT is behaving nonlinear. Chelating agents sequester the cations in formation brine or sea water and may change the wettability from oil wet to water wet. Hence more oil can be released from the reservoir. Decreasing trend of IFT could be due to the weakening of intermolecular forces at the oil/VES interface. While increasing trend of IFT at high temperatures could be due to inverse temperature effect on the solubility of surfactants [89].

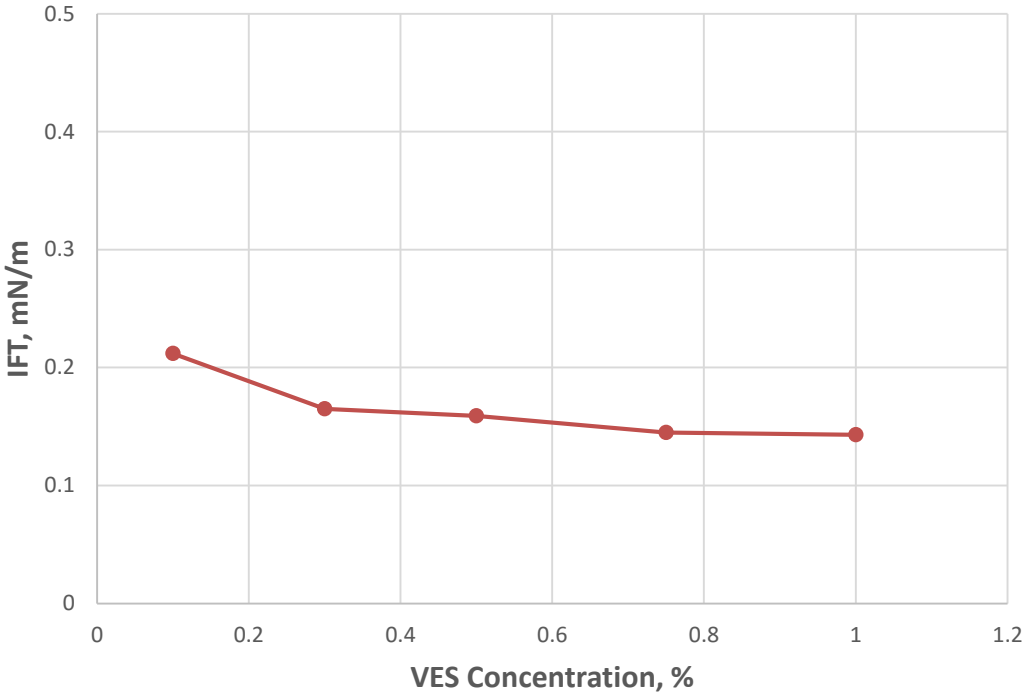

Figure 36: Effect of concentration on IFT of VES at 50^{o}C

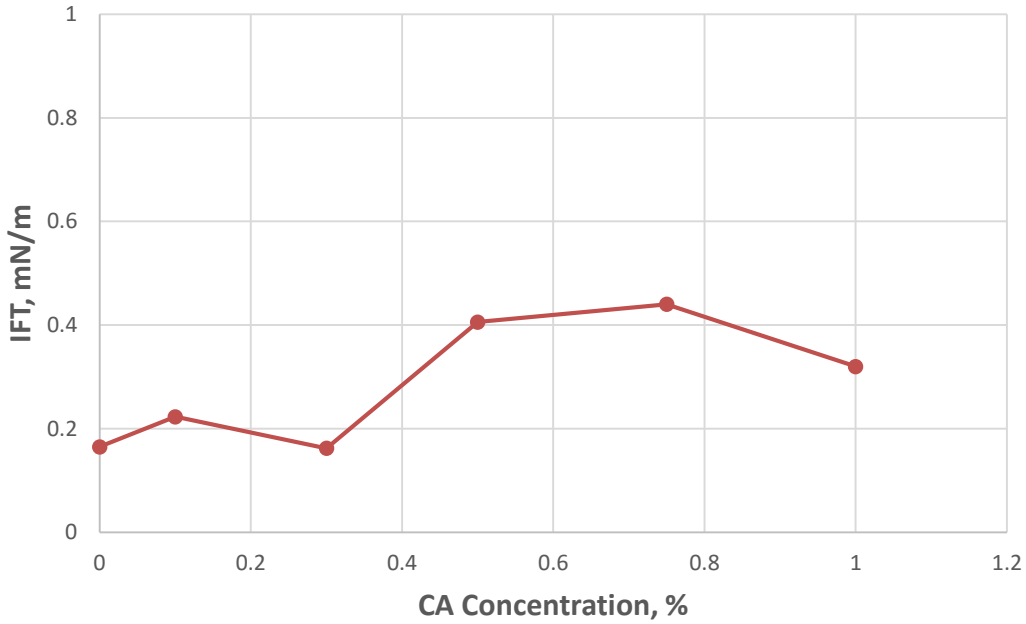

Figure 37: Effect of concentration on IFT of VES-CA at 50ºC

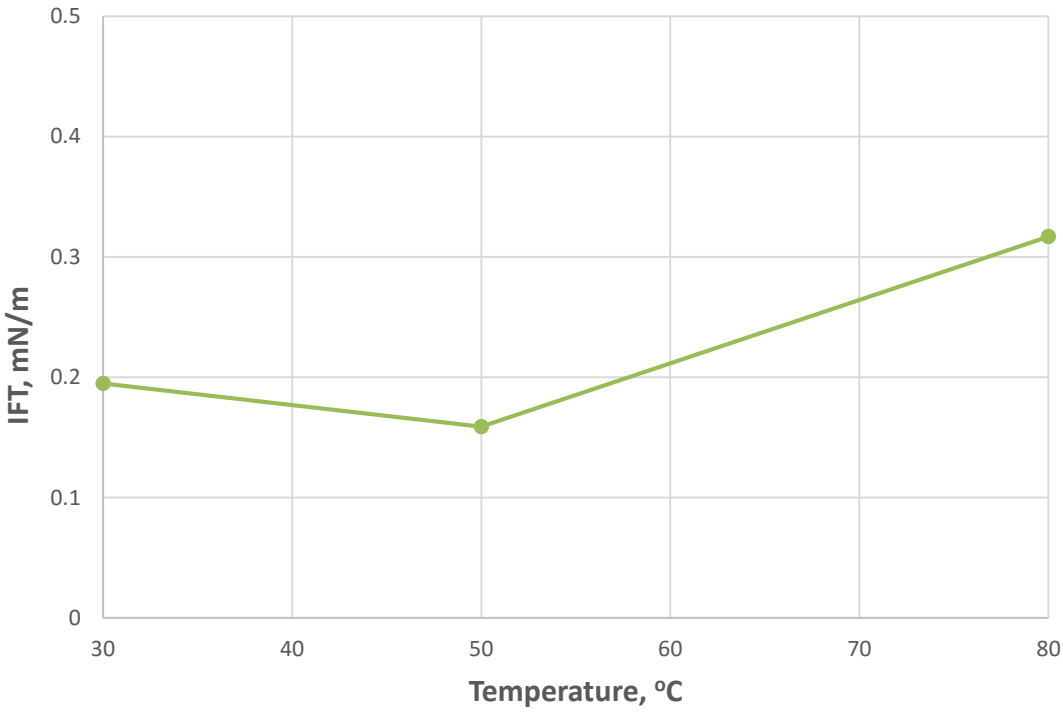

Figure 38: Effect of temperature on IFT of 0.5% VES

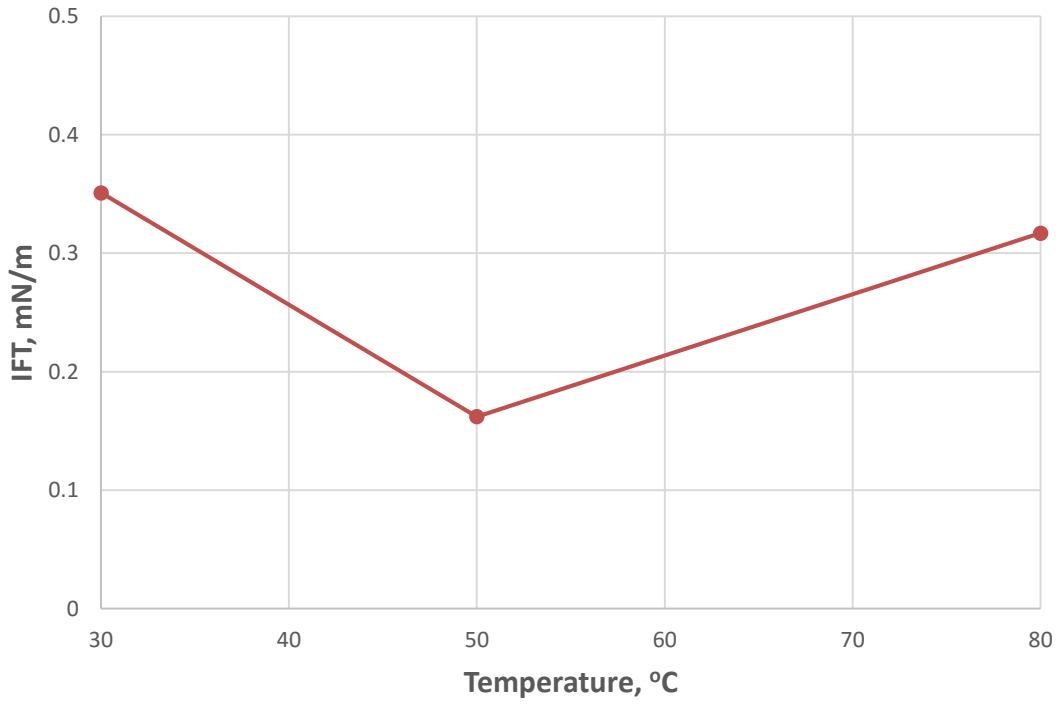

Figure 39: Effect of temperature on IFT of 0.3% VES-0.3% CA

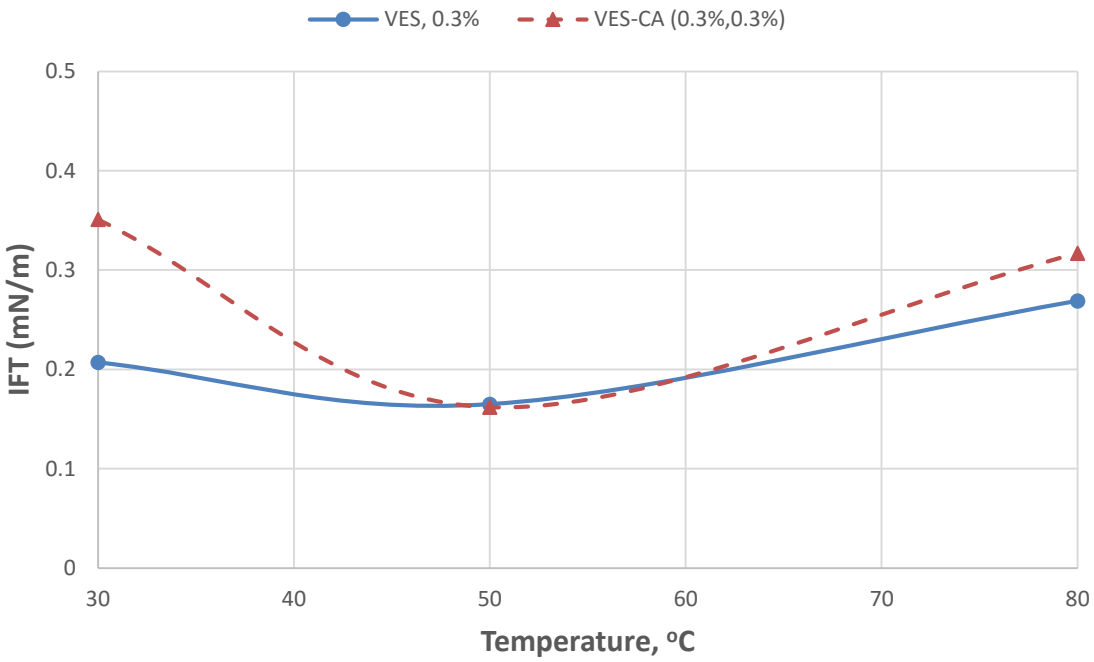

Figure 40: Effect of adding Chelating Agent on Temperature

4.7.4 Effect of Time

Interfacial tension of different VES concentrations from 0.1% - 1% is measured at 50^{o}C. Figure 41 shows the trend of IFT's measured with time. The time allotted for each measurement was 6000 secs. IFT initially increases or decreases in some cases and then stabilized at the long-time interval. The nonlinear behavior of IFT is due to light phase oil drop in spinning drop tensiometer. When the oil drop becomes stable, it attains a specific value of IFT at long time. Figure 42 shows the effect of adding chelating agent on IFT with time measured for 0.3% VES and 0.3% VES 0.3% CA at 50^{o}C. IFT for 0.3% VES shows some nonlinear trend and then stabilizes after some time. While the curve of 0.3% VES 0.3% CA gives stable value from the start. This usually depends when the oil drop becomes stable in the high dense phase inside the capillary of spinning drop tensiometer.

4.7.5 Viscosity/IFT Ratio

In EOR, viscosity of the fluid plays an important role in the recovery of oil from the reservoir. Mobility ratio and capillary number are the two main mechanisms that controls the oil recovery from the reservoir. Viscosity is the main factor in mobility ratio and IFT reduction is important to increase the capillary number. High viscosity increases the macroscopic forces while lower IFT reduces the microscopic capillary forces. Shear viscosity and IFT of various VES concentrations is presented in the Table 8. The test was performed at 30^{o}C. Viscosity/IFT ratio increases with the increase in concentration of VES solutions. Figure 35 gives the increasing trend of VES viscosity with the solution concentrations. Figure 43 gives the effect of concentration on IFT of VES at 30^{o}C.

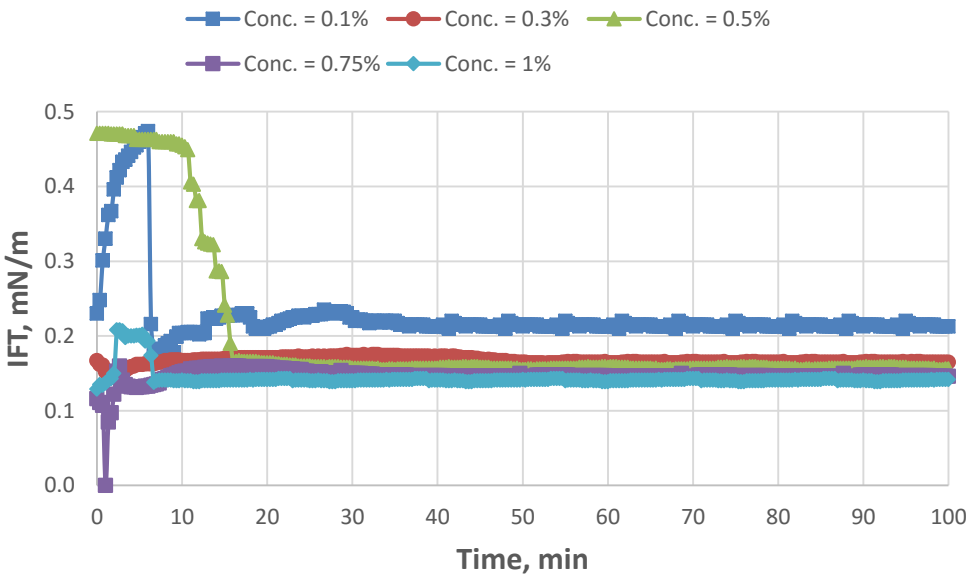

Figure 41: Effect of time on IFT of VES at 50^{o}C

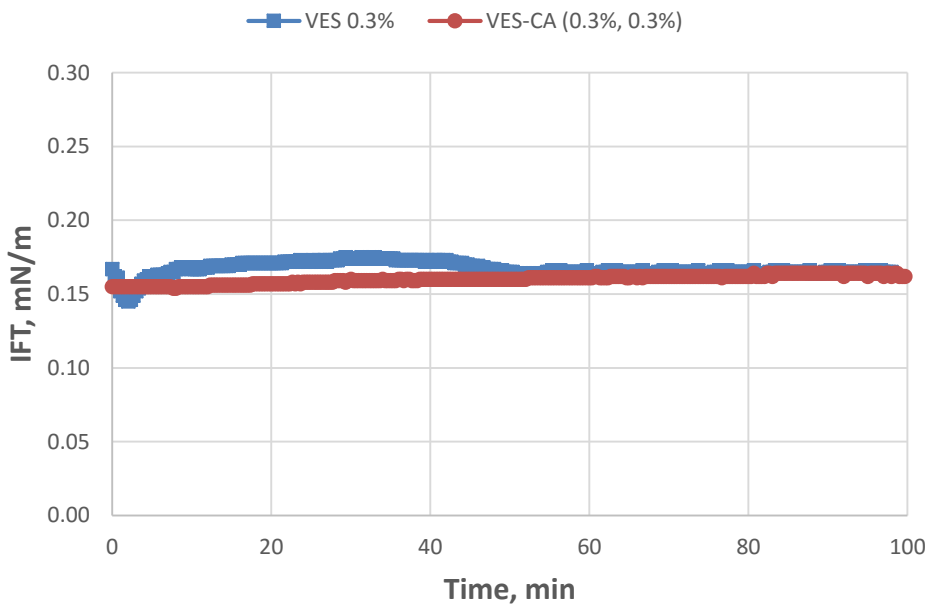

Figure 42: Effect of adding Chelating Agent on IFT with time at 50°C

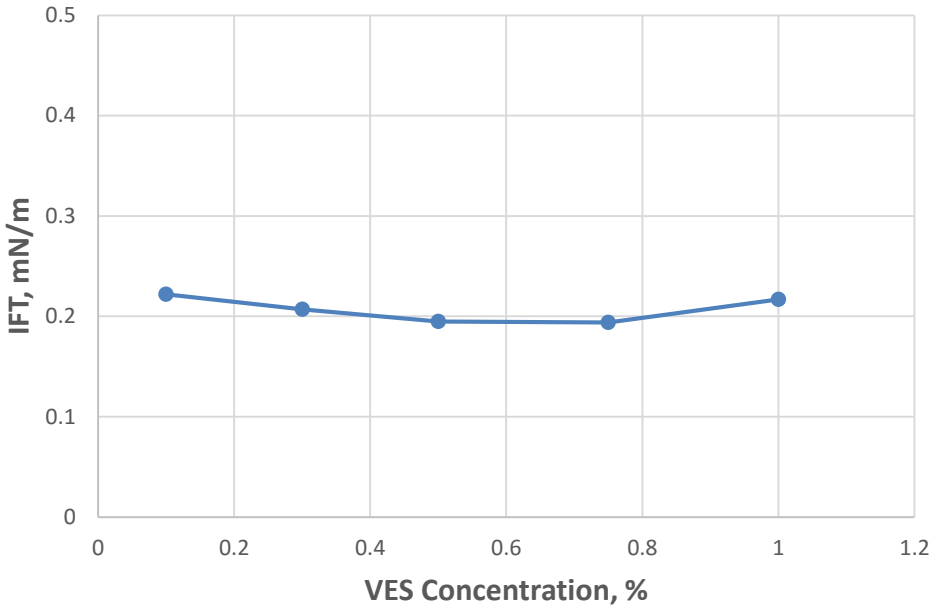

Figure 43: Effect of concentration on IFT of VES at 30°C

Table 8: Viscosity/IFT Ratio of VES at 30°C

Conc.	Shear Viscosity	IFT	Viscosity/IFT Ratio
wt %	cp	mN/m	cp/mNm^{-1}
0.1	4.637	0.222	20.889
0.3	23.690	0.207	114.448
0.5	31.986	0.195	164.033
0.75	48.465	0.194	249.819
1	93.800	0.217	432.2603

4.8 Thermal Characterization of VES

For the selection of any EOR mechanism, high temperature stability is the main factor that provides insight in the selection of injection medium. IFT and viscosity though provides the efficiency of the medium to recover more oil but sustaining the high temperature environment is a big issue. For this purpose, short term thermal stability tests are performed that evaluates the efficiency of the injection slug in high temperature environment. Also, the long term thermal stability tests are conducted to measure the potential of injection slug to retain its structure in such high temperature conditions. Hence thermogravimetric analysis and long-term aging results are presented in section 5.8.1 and 5.8.2. Solution preparation and the equipment used for short term thermal stability and long term thermal stability are given in section 4.1, 3.1.11 and 3.1.12 respectively. Different tests like IFT, viscosity, NMR and FTIR are performed with the aging samples to evaluate the thermal stability of the solution used. Aging is done at two different temperatures to study the applicability of optimum VES concentration as an EOR fluid to reservoirs of various temperatures.

4.8.1 TGA Analysis

Thermogravimetric analysis of viscoelastic surfactant was carried out using Thermogravimetric analyzer SDT Q600 TA instrument. Working principle and schematic are presented in previous section 3.1.11. Figure 44 shows the TGA curve for VES used for the study. VES showed high resistance to temperature until ~250^{o}C. Degradation of VES occurred in two stages. The first degradation step occurred from 250^{o}C to 375^{o}C that corresponds to the start of an autoxidation process and chain breaking reactions that leads to a weight loss of about 70%. The second step degradation of VES occurred from 375^{o}C

to 600^{o}C that could be linked to the secondary degradation reaction typical in the radical termination processes such as recombination reactions with a weight loss of 86% for VES. From the experimental results obtained with TGA it can be interpreted that VES has high thermal stability.

4.8.2 Long Term Aging

From the results of TGA, short term thermal stability of VES was evaluated. But in EOR, injection slugs need to be present in high temperature environment for some time. For that purpose, long term thermal stability tests were conducted to measure the potential of injection slug to retain its structure and mobility control effect in such high temperature conditions. The sample was prepared at 0.3% VES in sea water (57,642 ppm) and aged for 30 days. Solution preparation has been discussed in previous section 4.1.3. Two experimental setups were prepared to measure the long term thermal stability of VES at 90^{o}C and 120^{o}C separately. Different tests were conducted after taking the samples from the aged VES. Samples were taken at different time and run in FTIR, NMR, kinematic viscometer and IFT. Working principle and the schematic are described in section 3.1.12. Figure 45 below shows the samples collected before aging and Figure 46 shows the samples collected after the 30 days aging. For 90^{o}C the colour of the sample changed very less as compared to the original solution 0.3% VES used for aging. While the colour of sample for 120^{o}C collected after 30 days become yellowish. This may be due to the very high temperature and the dissolution of VES in the sea water.

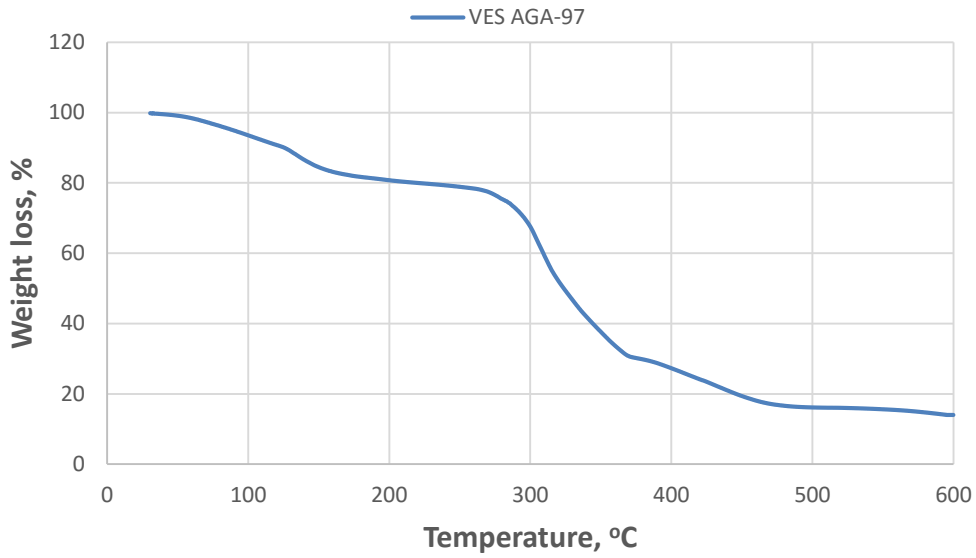

Figure 44: TGA curve of VES under nitrogen atmosphere at 10°C/min

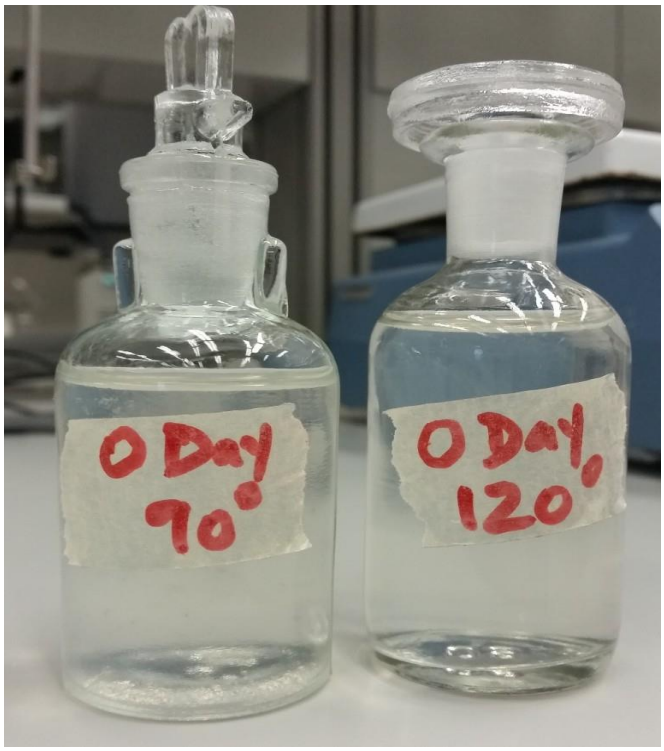

Figure 45: Samples of 0.3% VES before Aging

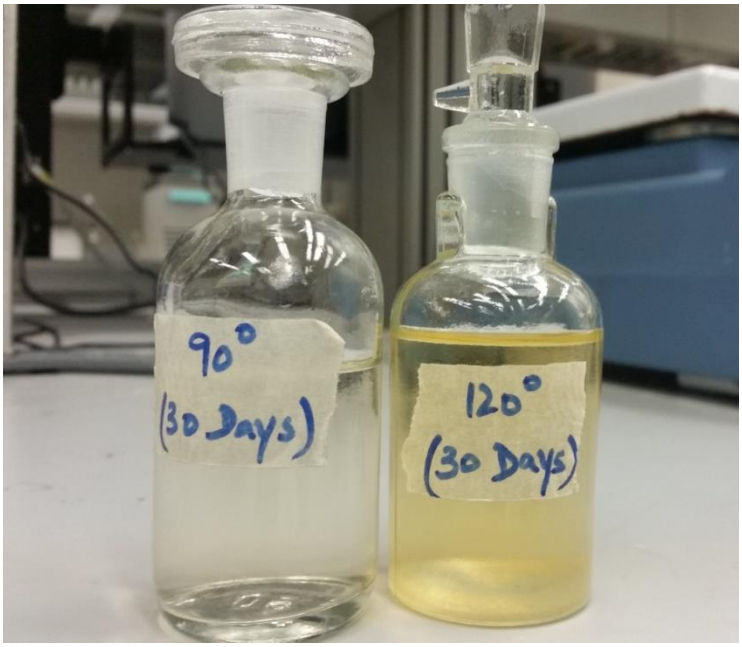

Figure 46: Samples of 0.3% VES after Aging for 30 days

IFT from Aged Samples

VES solution of 0.3% concentration was prepared in sea water of salinity 57,642 ppm and aged. Samples collected after aging the 0.3% VES for 30 days are analysed with IFT measurements. The aging of the samples was performed at two different temperatures of 90^{o}C and 120^{o}C. The time allotted for the IFT measurement was 6000 seconds. Figure 47 shows the IFT trends for 0.3% VES before and after aging. Samples of 90^{o}C and 120^{o}C are collected. IFT measurements are taken at 50^{o}C in spinning drop tensiometer. It is clear from the trend that after aging the samples at 90^{o}C and 120^{o}C, IFT increased about 4 times more than before aging. In the past, stabilizing agents have been used to improve the thermal stability of VES micelles, but particles may plug the reservoir pores and change the permeability of the reservoir. This enormous increase is due to the structural changes in the VES after exposing to high temperatures for aging that can be seen from the FTIR and NMR results. The effect of high temperature on IFT can be discussed in two reasons. The increase in temperature results in (a) favoring micellization due to the reduction of the degree of hydration of the hydrophilic groups and (b) inhibiting micellization due to the breaking of the water structure surrounding the hydrophobic groups.

Viscosity Measurements

Viscosifying ability of the VES solution samples collected after the aging is determined using kinematic viscometer. The working and schematic of viscometer is given in previous section 3.1.9. Viscosity of samples collected by aging 0.3% VES in sea water of salinity 57,642 ppm at 90^{o}C and 120^{o}C is presented in the Figure 48. Viscosity of the solution before aging was 23.69 cp but after aging solution viscosity reduces with time. This

reduction in viscosity can be due to the loss of WLM. Internal breakage of elastic VES has occurred at high temperatures of 90^{o}C and 120^{o}C.

FTIR Results

Thermal stability of VES is evaluated using Fourier transform infrared (FTIR) and NMR. FTIR spectra is obtained using a Bruker FTIR spectrometer as discussed in section 3.1.13. FTIR spectra of VES is presented in Figure 49 and Figure 50 for before aging and after aging samples at 90^{o}C and 120^{o}C. Frequency scale at the bottom of FTIR charts is given in cm^{-1}. Structural changes are identified in both FTIR spectra. It is seen that there is some change around 3300 cm^{-1} in both spectra where an OH group may be present and H-bonding leads to broadening. Because of high temperature the intensity of FTIR in this region has changed. It may be due to the removal of water particles from the non-aged sample that are lost in the aged samples FTIR. There is no change around 1600 cm^{-1} in both the spectra where C=O group is present, and it is strong in that region. Two peaks are visible in the region of 1050-1150 cm^{-1} at 90^{o}C while one peak is visible before aging at 120^{o}C and two peaks after the aging where O-C has medium to strong intensity. Also, there is some change in the region 600-700 cm^{-1} which could be due to the C-H bond deformation in both the spectra.

NMR Results

NMR analysis is performed to further evaluate the structural changes. Samples for NMR analysis are prepared in 5 mm NMR tubes using D_2O. JEOL 500 MHz spectrometer is used to obtain NMR spectra of VES before and after aging. Several scans are performed to collect the ^{1}H NMR (proton NMR) and ^{13}C NMR (Carbon NMR). ^{13}C NMR gives us the carbon backbone of a molecule, which is incredibly useful when we are trying to figure out

the structures of organic substances. ^{1}H NMR and ^{13}C NMR spectra for VES at 90^{o}C before aging and after aging is shown in Figure 51 and Figure 52 respectively. It can be observed that all the peaks for ^{1}H NMR lie in the aliphatic region and due to the presence of O-C bond the peaks are shifted forward. While from the ^{13}C NMR, it is observed that carbon peaks are in the aliphatic region and their intensity has changed. It could be due to the high temperature or difference in the amount of sample used for the determination of NMR. ^{1}H NMR and ^{13}C NMR spectra for VES at 120^{o}C before aging and after aging is shown in Figure 53 and Figure 54 respectively.

4.9 Rheological Characterization

Rheological study is carried out to study the change in the flow and form of elasticity and viscosity. Viscosity is the measurement of fluid flow friction. Viscosity measurements provide necessary information about the material depending on the rate at which is being sheared. Non-Newtonian fluids have another characteristic of changing their viscosity as the shear rate is increased or decreased. Shear thinning is a phenomenon when the fluid viscosity decreases with increase in the shear rate. Effects of shear rate and effects of step time are discussed in the next sections. The chemistry of VES and the addition of chelating agent to VES has been studied.

4.9.1 Effect of Shear Rate

The more viscous the fluid, the more is the force required to move the fluid and that is called shear force. Figure 55 shows the effect of shear rate on viscosity of VES. The concentration of VES used for this experiment is 0.3%. Solution preparation is discussed in previous section 4.1.3. The temperature applied for the measurement is 90^{o}C. It is clear

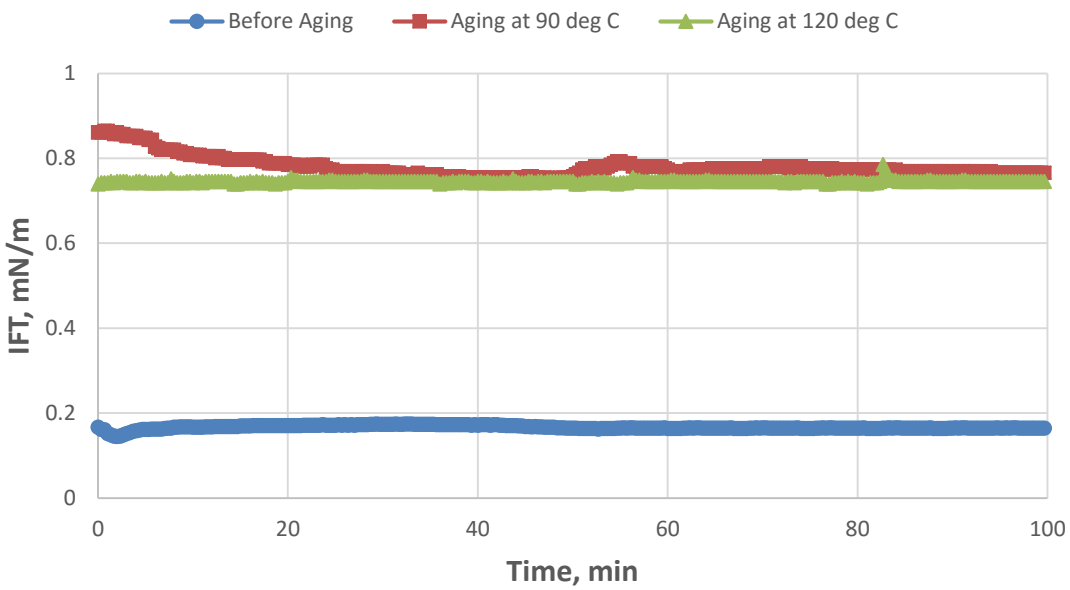

Figure 47: Effect of aging on IFT of 0.3% VES with time

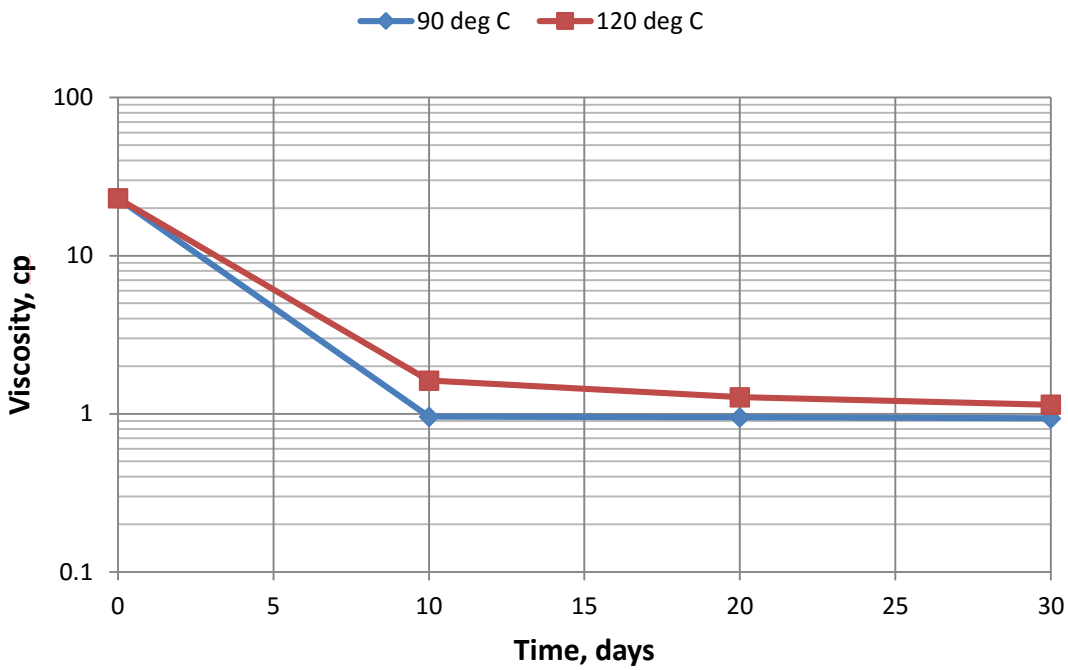

Figure 48: Viscosity of 0.3% VES after aging with time

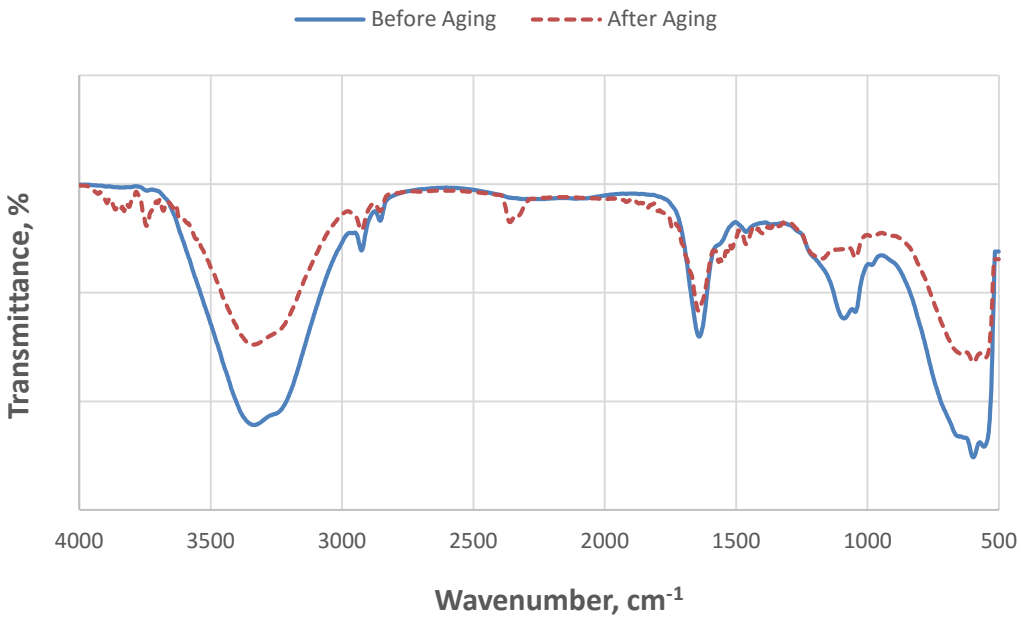

Figure 49: FTIR of 0.3% VES at 90°C

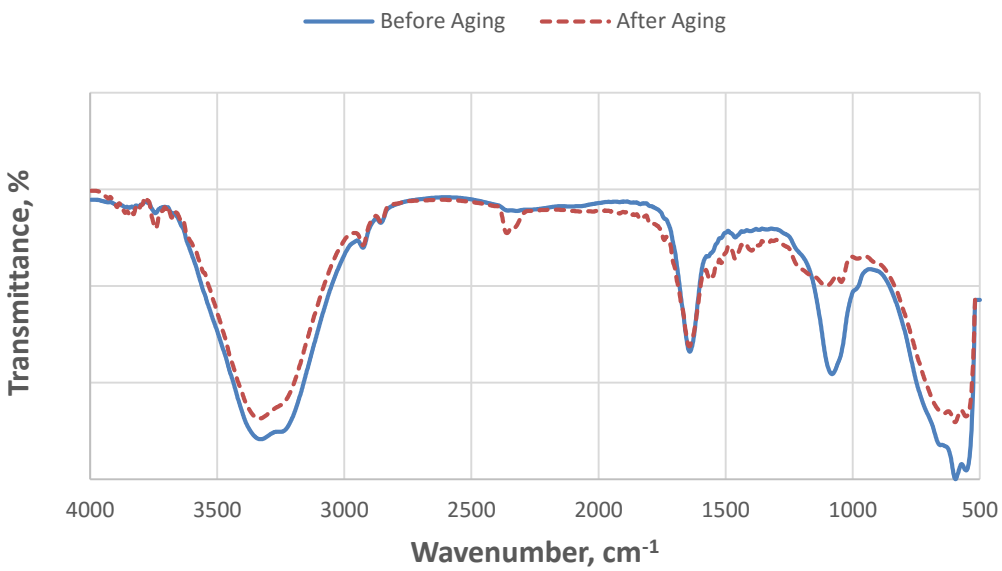

Figure 50: FTIR of 0.3% VES at 120ºC

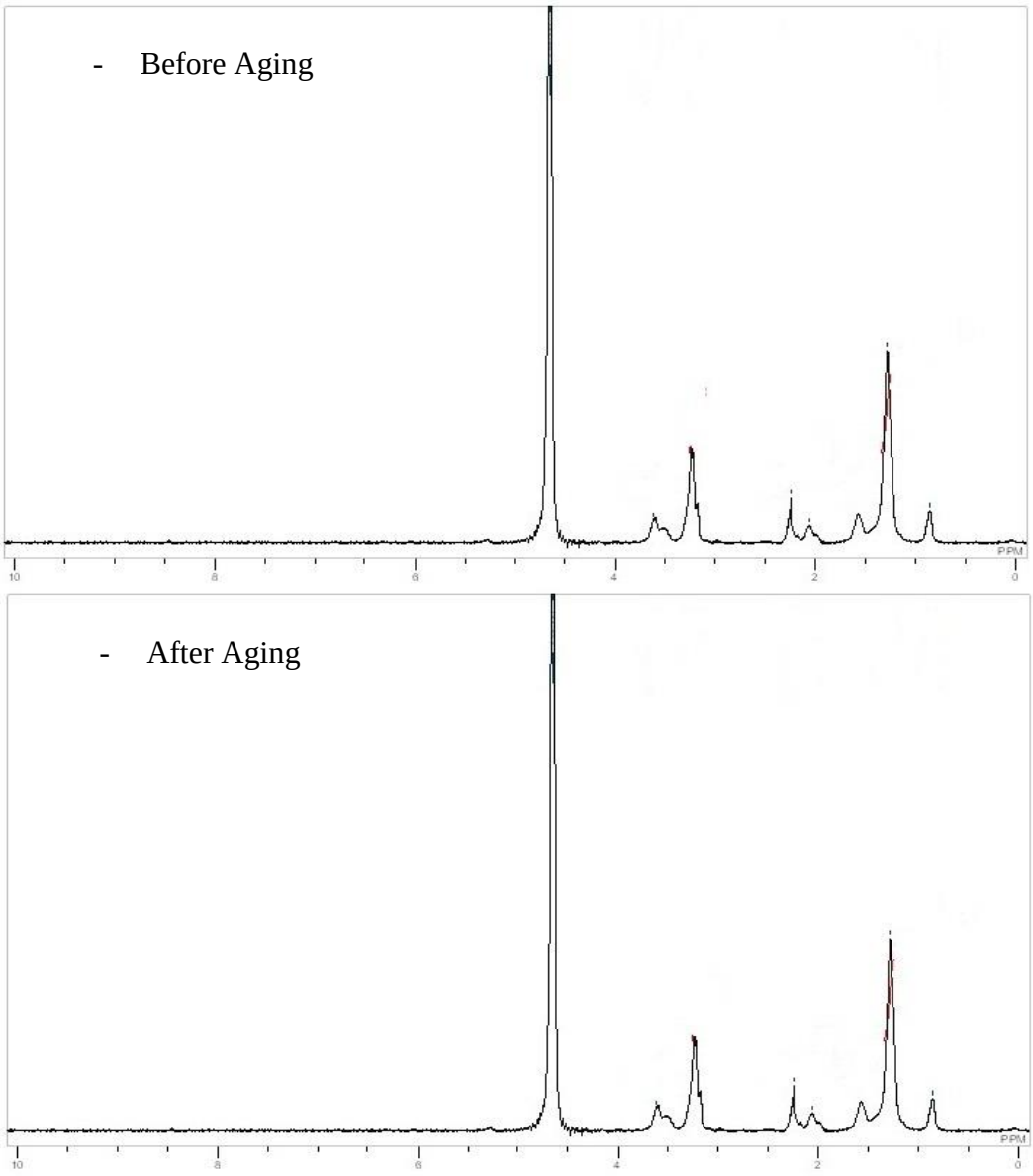

Figure 51: ^{1}H NMR spectra for VES at 90^{o}C before aging and after aging

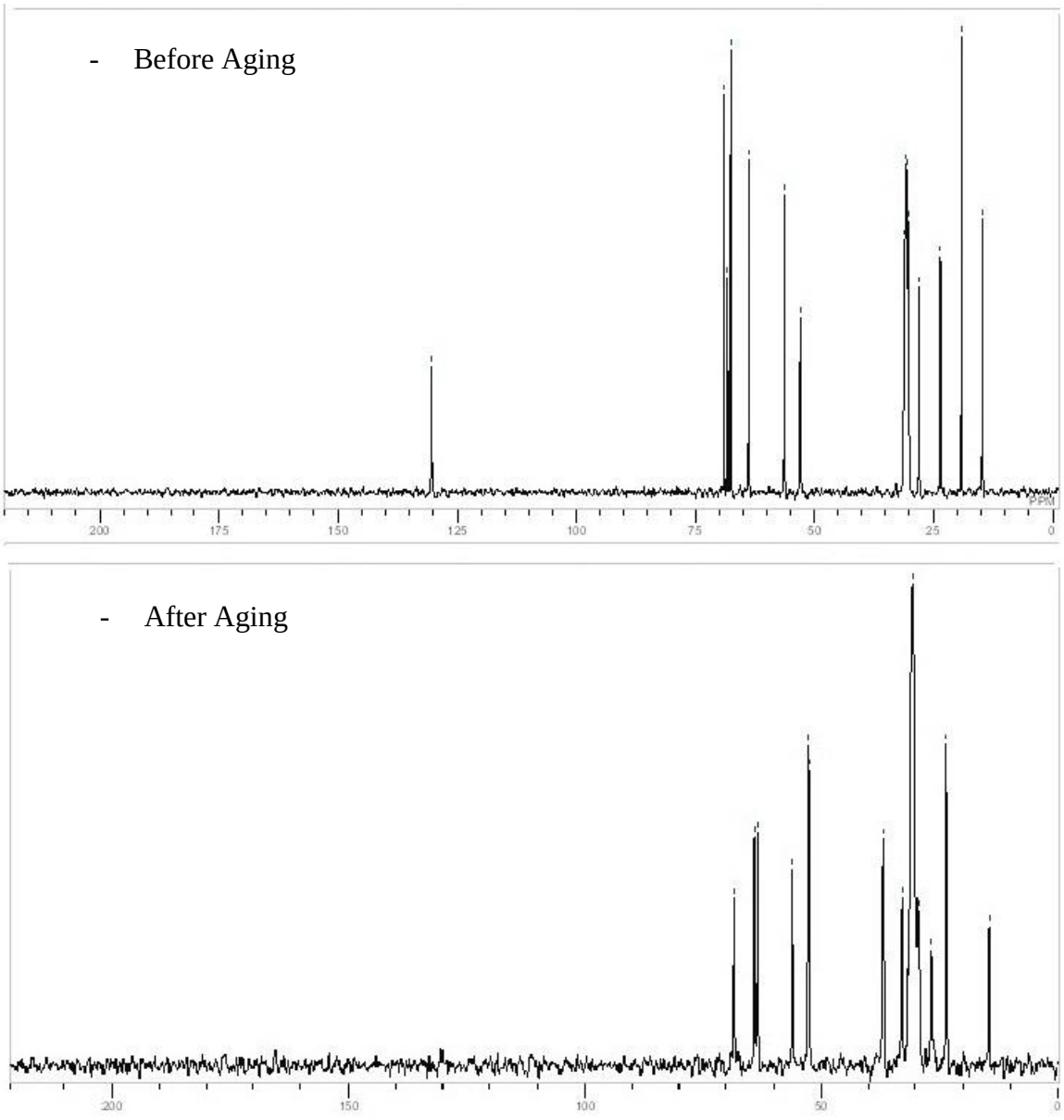

Figure 52: ^{13}C NMR spectra for VES at 90^{o}C before aging and after aging

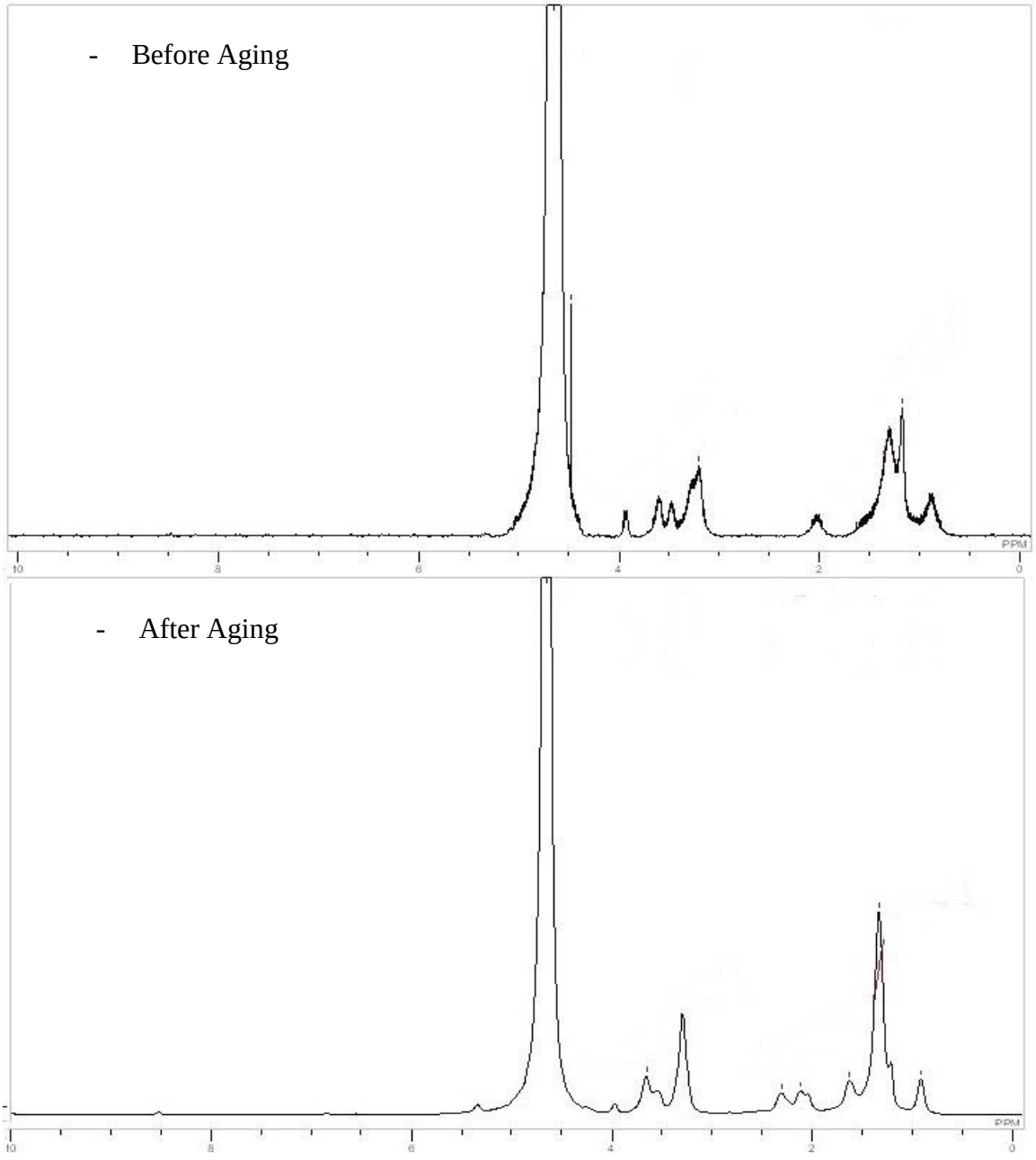

Figure 53: ^{1}H NMR spectra for VES at 120^{o}C before aging and after aging

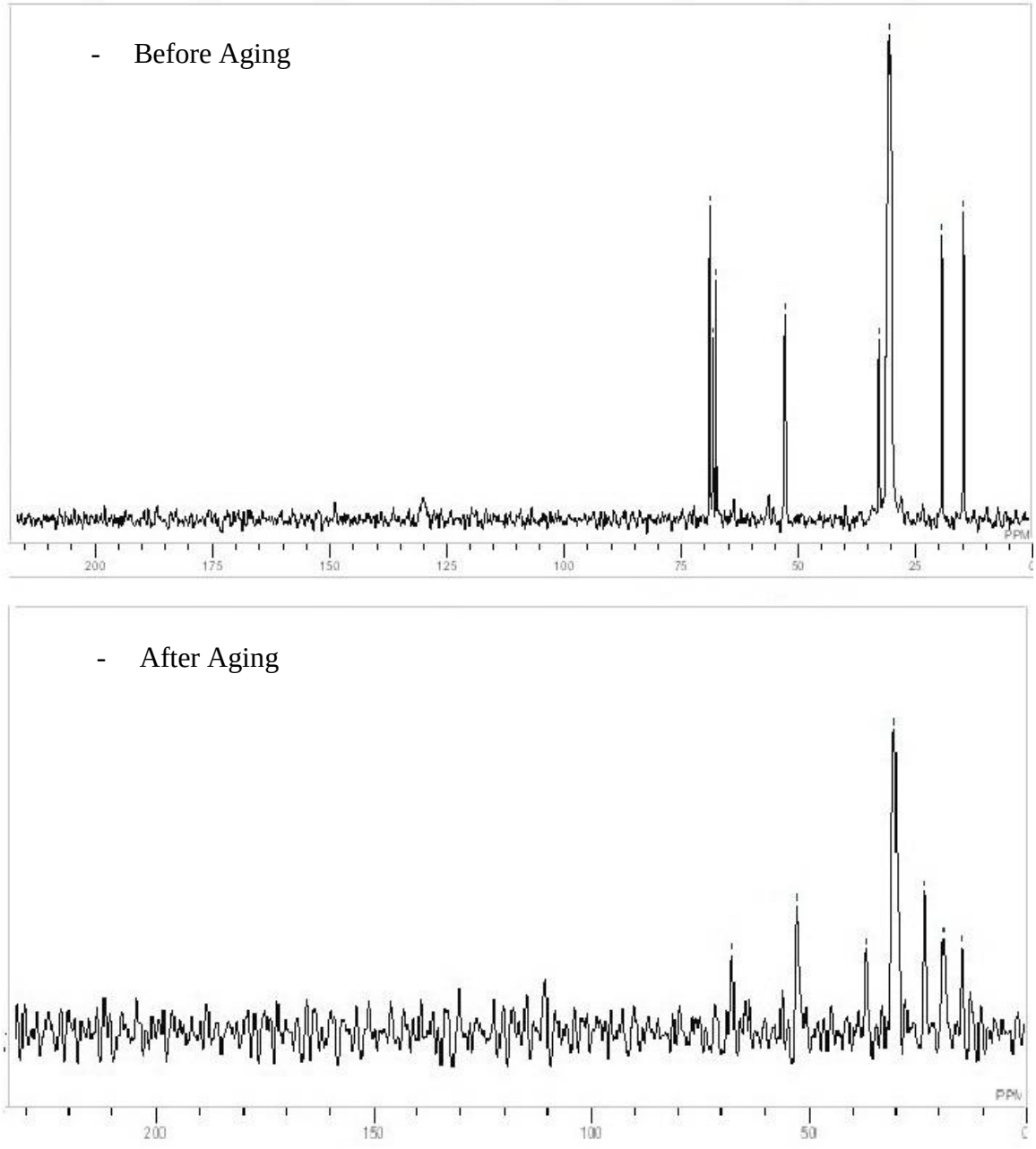

Figure 54: ^{13}C NMR spectra for VES at 120^{o}C before aging and after aging

from the trend that viscosity is decreasing with increase in shear rate. It means VES is undergoing shear thinning at 90^{o}C. Viscosity decreases until shear rate of 2s^{-1} and then becomes constant. Temperature has an impact on the viscosity measurements. The effect of elasticity has reduced with high temperature of 90^{o}C. Decrease in viscosity is due to the interaction of counter ions with the elastic part of VES. Figure 56 shows the effect of shear rate on viscosity of VES-CA solution. The concentration of VES used for this experiment is 0.3% and for chelating agent is also 0.3%. Solution preparation is discussed in previous section 4.1.3. The temperature applied for the measurement is 90^{o}C. It is clear from the trend that viscosity is decreasing with increase in shear rate. It means VES is undergoing shear thinning at 90^{o}C.

4.9.2 Effect of time

Under high temperature conditions viscoelastic fluids undergo changes with time. Figure 57 presents the effect of time on viscosity of VES. The concentration of VES used for this experiment is 0.3%. Solution preparation is discussed in previous section 4.1.3. The temperature applied for the measurement is 90^{o}C. It is clear from the trend that viscosity decreases initially and then it stabilizes. The viscosity measurements are taken at constant shear rate of 7s^{-1}. The time allotted for the measurement is one hour. Values obtained for the viscosity from rheometer are plotted against step time. Viscosity changes occur until 25 min and then becomes constant at the value of 15 mPa.s. The friction between the two layers of fluid becomes apparent when one layer tries to move relative to the other layer. Figure 57 also presents the effect of time on viscosity of VES and chelating agent. The concentration of VES used for this experiment is 0.3% and the concentration of cheating agent is 0.3%. The temperature condition is same 90^{o}C as used for VES. The test was

carried out for 1 hour to let the viscosity value stabilize for some time. It is observed that the viscosity decreases to a certain value and then stabilizes. The value of viscosity obtained with VES-CA solution is less as compared with the VES solution. This is the indication that at high temperatures VES gives more viscosity than the VES-CA solution. More viscosity means mobility ratio is good and better will be the sweep efficiency in the reservoir.

4.10 Static Adsorption Measurements

Adsorption is a phenomenon in which molecules of the surfactant are transported from bulk phase to the solid-liquid interface. Static adsorption plays an important role in the screening of EOR process. It also determines the efficiency of the injected fluids on the oil recovery. Orientation of the structure of the formulation injected determines how the interface will react towards adsorption. The behavior of surfactants at the interface is determined by number of forces, including electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation of various species[91]. Static adsorption of VES is carried out to determine the efficiency of VES to recover oil. The adsorption of VES play a dual role in the removal of oil. It reduces the attraction between oil and rock by attaching itself to both and reside on the interface of oil and mineral surface. Static adsorption can happen in the form of monomers as single layer adsorption at low concentrations of VES used and also in the form of micelles like structures where monomers tend to aggregate and form bilayers at high concentrations of VES used. Depending on the number of layers for aggregated monomers, the micelles are called admicelles for one layer and hemimicelles for two layers[73] and [91]. As the number of layers increase and the adsorption approaches the plateau value, the rate of adsorption

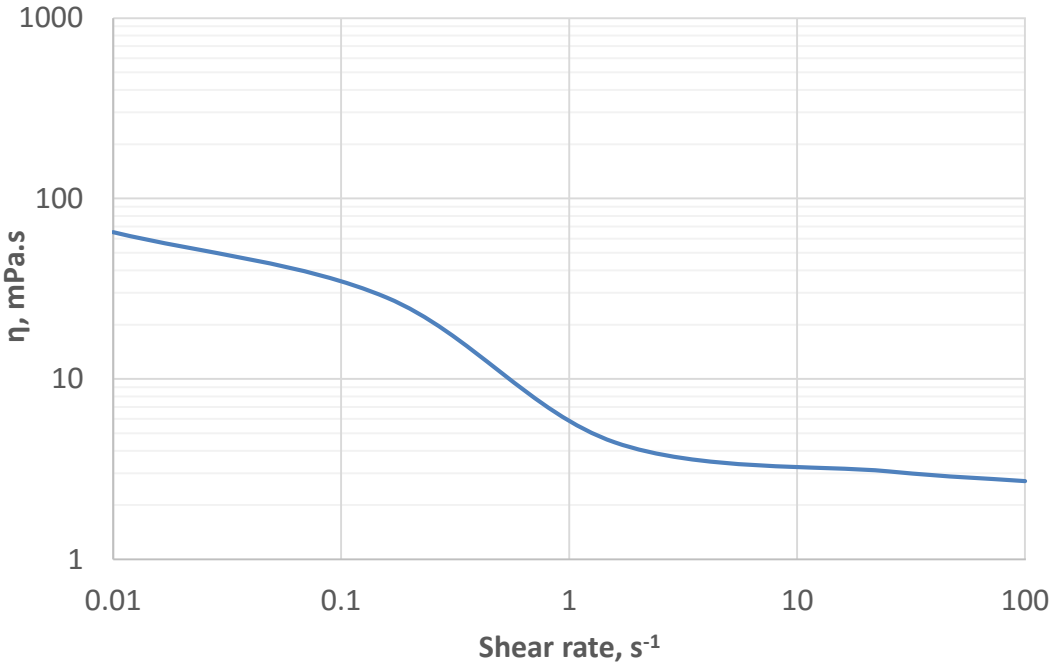

Figure 55: Effect of shear rate on viscosity of 0.3% VES at 90°C

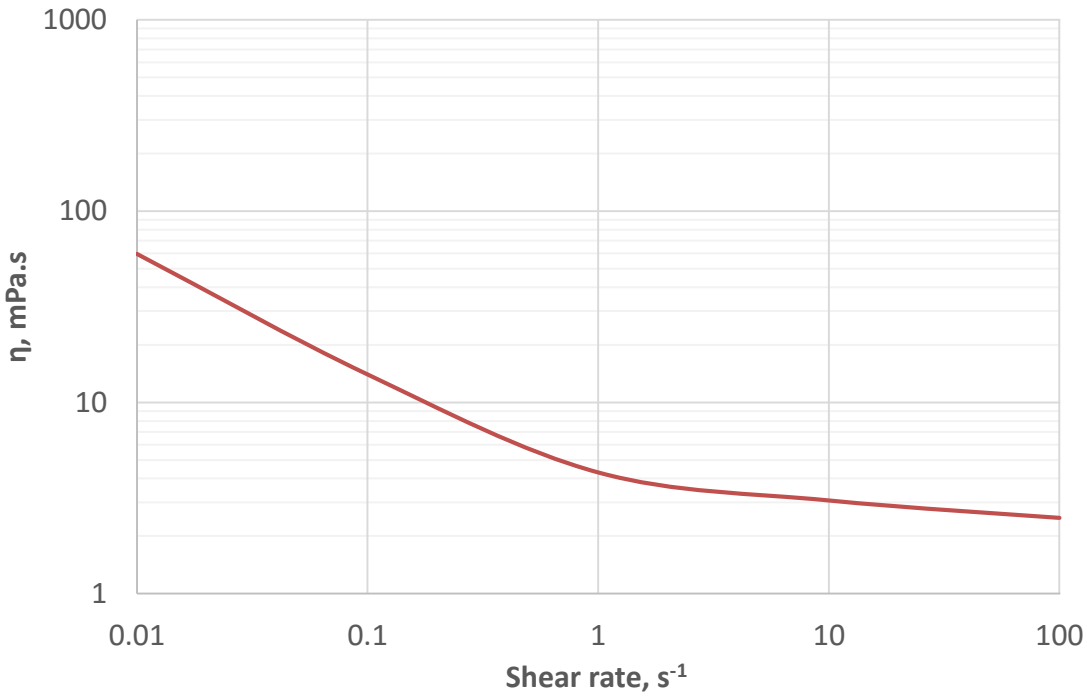

Figure 56: Effect of shear rate on viscosity of 0.3% VES - 0.3% CA at 90°C

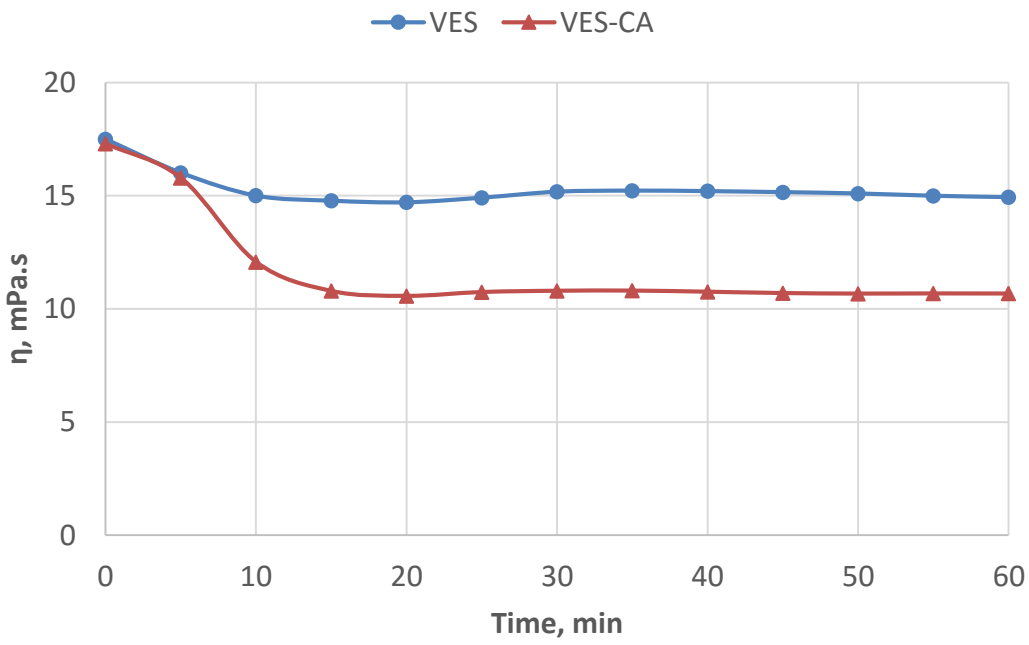

Figure 57: Viscosity vs time for VES and VES-CA at 90ºC

begins to decrease. At high temperature conditions adsorption of VES is less as compared to low temperature conditions. Many authors have presented their work on adsorption of surfactants and it can be summarized that three regions are present in adsorption measurements i.e. linear region, transition region and the plateau region. The range of each region depends on the mineral surface and the concentration of surfactant used. Adsorption kinetics also depends on the electro interactions of VES and the mineral surface. Adsorption studies are carried out at two different temperatures of 30^{o}C and 60^{o}C.

4.10.1 Concentration Analysis

Adsorption of VES is carried out to determine the effect of adsorbent on the sorption efficiency. VES solutions are prepared of concentrations from 0.01-0.1% with sea water of salinity 57,642 ppm and their static adsorption on the crushed powdered sample is determined. Solution preparation has been already discussed in section 4.1.3. Detailed procedure for the adsorption analysis is described in section 4.6. Solutions are prepared and analyzed for concentration measurements. Solid to liquid weight ratio used was 1:15. The ratio is selected based on the previous work in literature. 2g of crushed carbonate samples are added to a 30mL solution of VES. The prepared samples after treating are centrifuged for 15 min at 10,000 rpm. Adsorption studies are assessed using Total Organic Carbon (TOC) analyzer for concentration analysis. Calibration curve is plotted between the VES concentration and the TOC values as presented in Figure 59. Linear trend is obtained which shows the increment in the TOC values with the increase in concentration of VES. Straight line equation is determined and is used further to calculate the adsorption. The supernatant samples after the shaking and equilibrium at required temperature are taken and analyzed with TOC analyzer and used in the straight-line equation to determine

the corresponding concentration. The difference between the initial concentration and final concentration is determined and the adsorption is calculated using the following relation:

$$q = \frac{m_{VES}(C_i - C)}{m_{rock}} * 10^{-3} \quad (7)$$

Where,

q = Adsorption on rock surface, mg/g-rock

m_{VES} = mass of VES solution treated with rock sample, g

m_{rock} = mass of rock treated with VES solution, g

C_i = Initial concentration of VES before treatment, wt%

C = Final concentration of VES after treatment, wt %

4.10.2 Effect of Temperature on Static Adsorption

Adsorption is calculated at two different temperatures of 30°C and 60°C and at atmospheric pressure. Results are presented in Figure 60. Adsorption density is greater with 30°C and less with 60°C. So, high temperature reduces the adsorption. The trend is increasing with the increase in concentration of VES. Low concentrations of VES are used to determine adsorption on the rock surface. This may be due to the reduction in viscosity of VES at high temperature. Changes in the surfactant concentration during the adsorption tests are determined using TOC. Adsorption density vs equilibrium surfactant concentration is presented in Figure 64.

4.10.3 Conductivity Measurements for CMC

In this research, conductivity method is used to perform CMC measurements. VES solutions are prepared of concentrations from 0.1-10wt% with deionized water.

Conductivity of the solutions is measured from high concentration to low. Solution preparation has been already discussed in section 4.1.3. Conductivity meter from OARTON is used to measure the conductivity of solutions. The conductivity meter is calibrated with the standard solution and then used for the measurements of VES solutions. Every time the electrode is cleaned with DI water to ensure accurate measurements. Measurements obtained from the conductivity meter are plotted in a graph presented in Figure 61. It clearly shows that by increasing the concentration of VES the conductivity value increases. CMC obtained is at 3% where the slope of the line changes.

4.10.4 Langmuir Isotherm Model

Having adsorption measurements with the VES solutions of different concentrations, a model is required to predict the loading on the adsorption matrix at a certain concentration of the component. Adsorption data is examined using Langmuir isotherm which is obtained under totally homogeneous adsorption surface. Figure 58 displays the schematic of Langmuir model. Langmuir model assumes[92];

1. Monolayer coverage only.

2. Equilibrium model.

3. All adsorption sites are perfectly flat plane.

4. There are no interactions between adsorbate molecules on adjacent sites.

Adsorption parameters using the Langmuir model are determined. Equation defining his model is given below as:

$$q_e = \frac{q_o K_{ad} C_e}{1 + K_{ad} C_e} \quad (8)$$

Where,

q_o = Maximum adsorption capacity for forming single layer, mg/g

Ce = Equilibrium concentration of solute remaining in the solution, mg/L

q_e = Equilibrium adsorption rate, mg/g-rock

K_{ad} = Constant of adsorption reaction, L/mg

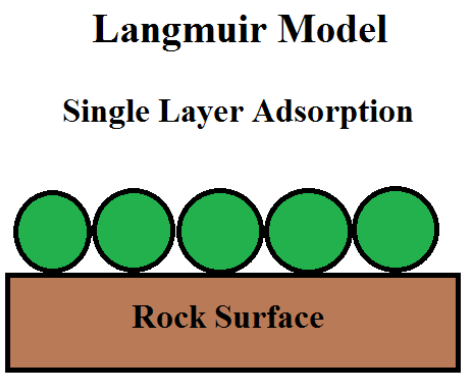

Figure 58: Schematic of Langmuir Model

Thus, a plot of 1/qe vs 1/Ce will give a straight line if the Langmuir isotherm is obeyed by the adsorption equilibrium. From the slope and intercept of the straight line, q_o and K_{ad} values are calculated respectively. Adsorption experiments are performed at 30^{o}C and 60^{o}C. Results obtained from Langmuir isotherm model are plotted with experimental data presented in Figure 63 and Figure 64 for both temperatures. The difference between both isotherms is clear. The experimental results fit good with the Langmuir model. Low concentrations of VES are used for experiment data so the linear trend of Langmuir curve is matching. The trend of Langmuir is extended for higher concentrations using the same model as with our experimental data. Rate of adsorption increases linearly with VES concentrations in the initial region. Wayman and Scamehorn studied the adsorption of surfactant on various clay minerals. They concluded that the adsorption isotherms match the Langmuir equation[93] and [94].

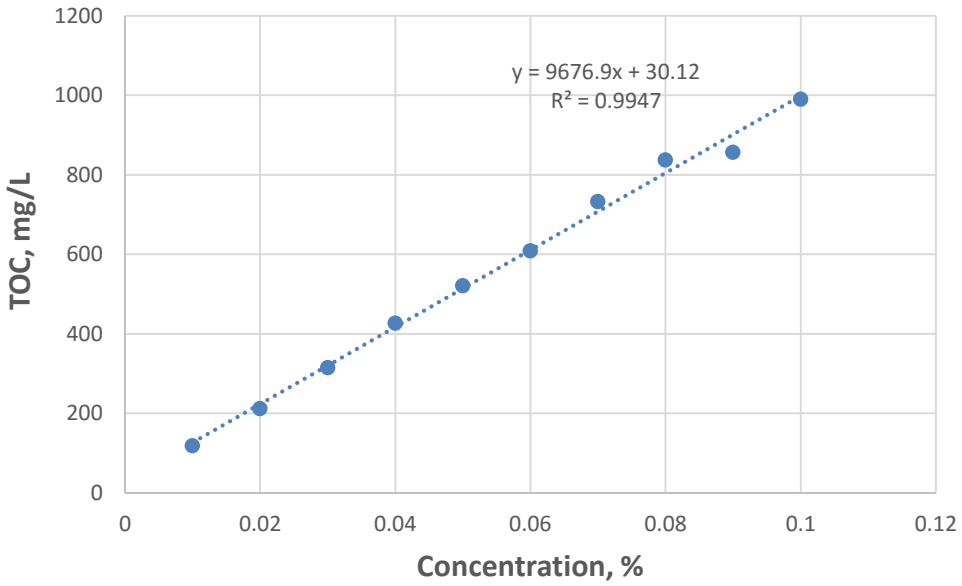

Figure 59: Calibration curve at different concentrations of VES using TOC

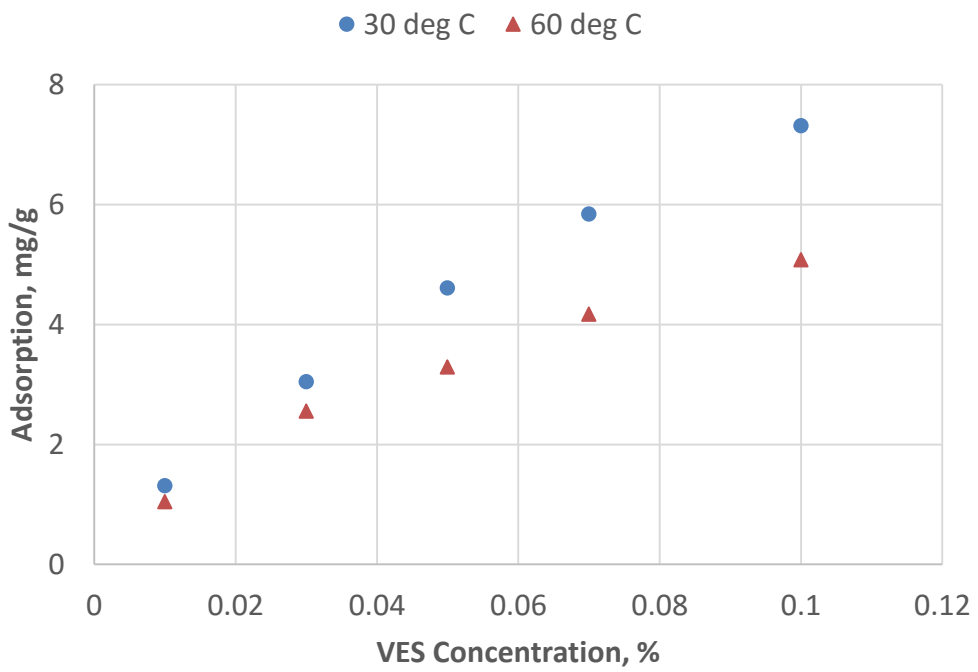

Figure 60: Effect of concentration on adsorption of VES at 30ºC and 60ºC

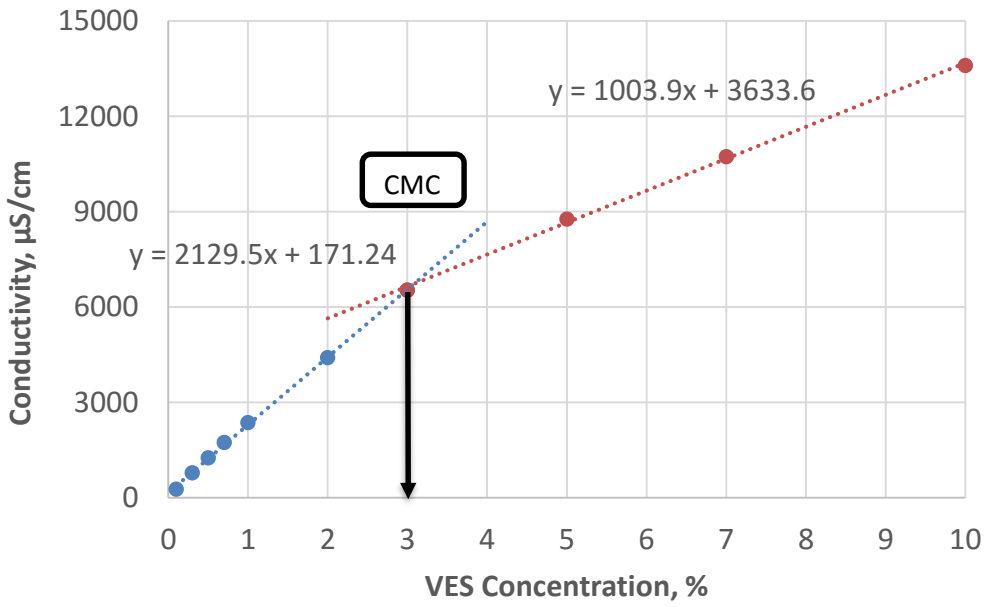

Figure 61: Conductivity measurements of VES concentrations in DI water

4.10.5 BET Isotherm Model

Brunauer–Emmett–Teller (BET) theory is the extension of Langmuir model. The first multilayer adsorption was introduced by BET whereas Langmuir only considers monolayer adsorption[95]. Figure 62 shows the schematic for BET model. They assume the following:

1. Langmuir theory can be applied to each layer.
2. Gas molecules physically adsorb on a solid in infinite layers.
3. There is no interaction between each adsorption layer.

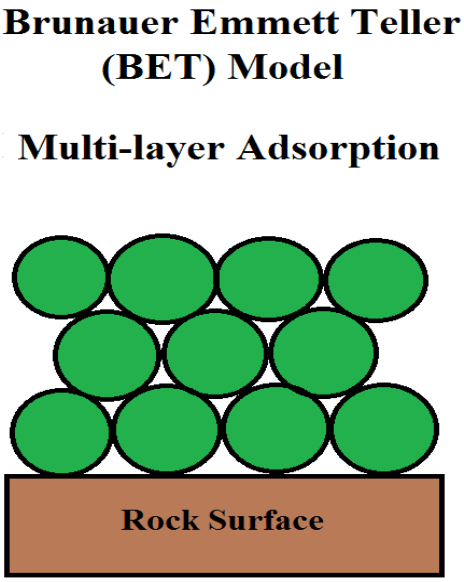

Figure 62: Schematic of BET model

For the BET isotherm, we can arrange the equation as:

$$\frac{C_e}{(Cs-Ce)*qe} = \frac{K_B-1}{K_B*q_o}\frac{Ce}{Cs} + \frac{1}{K_B*q_o} \quad (9)$$

Where,

q_o = Maximum adsorption capacity for forming single layer, mg/g

Ce = Equilibrium concentration of solute remaining in the solution, mg/L

q_e = Equilibrium adsorption rate, mg/g-rock

K_B = Parameter related to binding intensity of all layers, L/mg

Cs = Saturation concentration of solute, mg/L

Thus, a straight line is obtained and the slope and intercept are determined to calculate the remaining parameters.

$$Slope = \frac{K_B - 1}{K_B * q_o * Cs}$$

$$Intercept = \frac{1}{K_B * q_o}$$

Adsorption experiments are performed at 30°C and 60°C. Results obtained from BET isotherm model are plotted with experimental data presented in Figure 63 and Figure 64 for both temperatures. The difference in both the isotherms is clear. The experimental results fit good with the BET model at the initial linear trend. Low concentrations of VES are used for experiment data so the linear trend of BET curve is matching. The trend of BET is extended for higher concentrations using the same model as with our experimental data. BET adsorption isotherm shows large deviation from the Langmuir adsorption model.

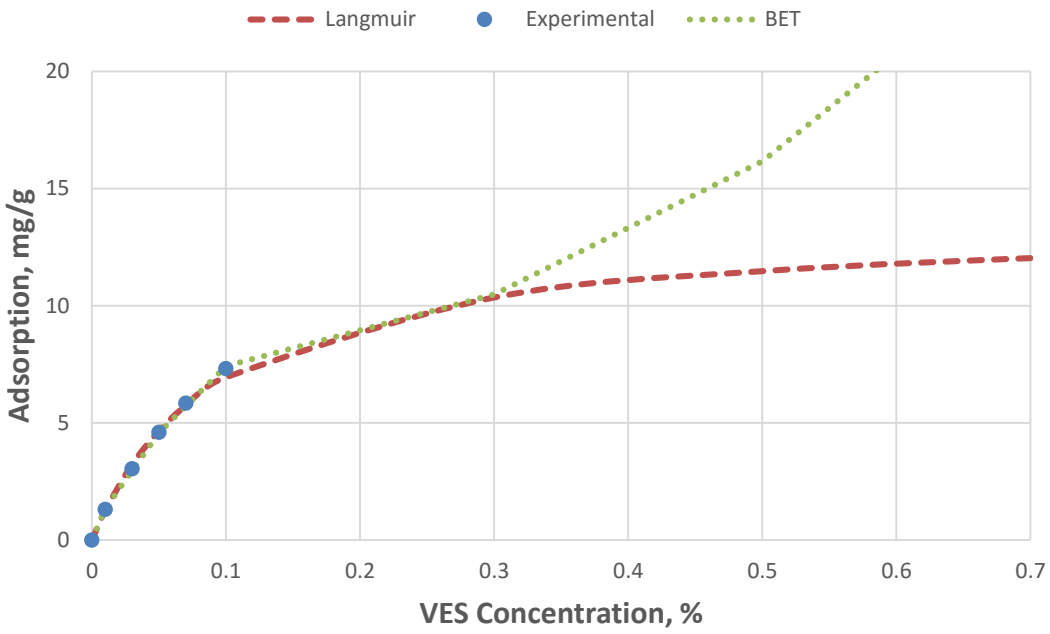

Figure 63: Langmuir and BET comparison at 30°C

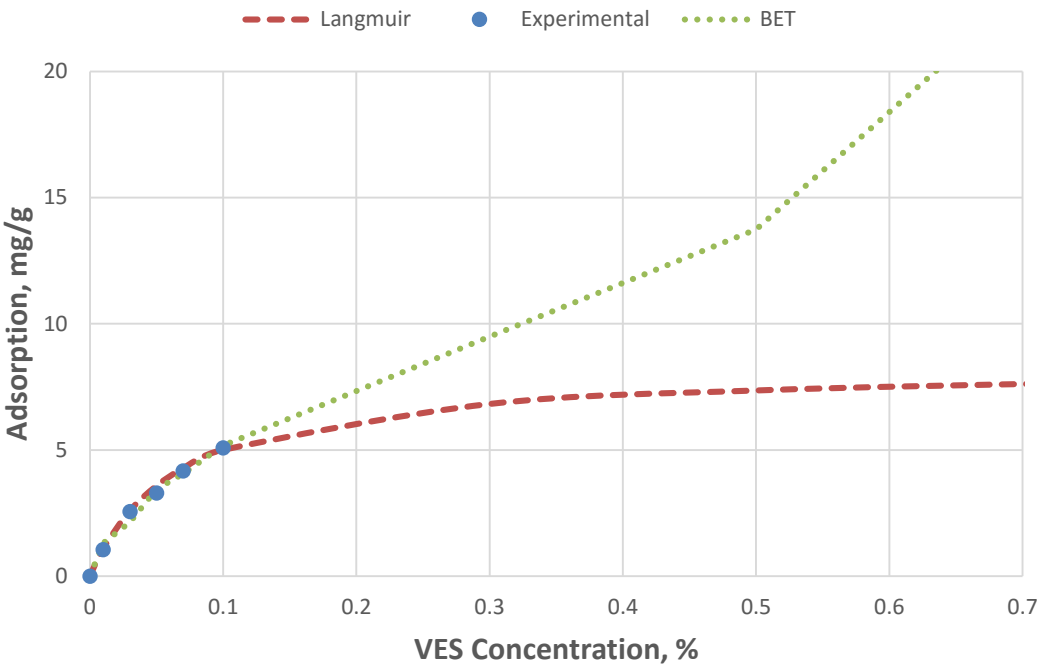

Figure 64: Langmuir and BET model comparison at 60°C

4.11 Zeta Potential Measurements

Most of the carbonate reservoirs are characterized by high temperature and high salinity. Carbonate reservoirs contain high concentration of divalent ions**.** From XRD and XRF analysis about 98% Ca ions are present given in section 5.3. At high temperature, the surfactant tends to precipitate upon exposure to divalent cations and will partition to the oil phase at high salinities. These carbonate reservoirs require specially formulated chemicals system which could mitigate the above problems. Employing VES in our system was sought to address these problems. Viscoelastic surfactant combines both elastic and viscous properties. Zeta potential measurements help in determining the ability of VES and VES-CA solutions to move the oil from the surface of carbonate rock. Effect of VES and VES-CA solutions prepared in sea water has been studied on zeta potential measurements.

4.11.1 Effect of VES Solutions

Zeta potential measurements between VES solutions of different concentrations and powdered rock from Wafra Ratawi formation is presented in Figure 65. VES solutions are prepared of concentrations from 0.1-1% with sea water of salinity 57,642 ppm and their zeta potential is determined. Solution preparation has been already discussed in section 4.1.3. Low concentrations of VES are used for zeta potential measurement to study the effect of adsorption. All zeta potential measurements are performed at 25^{o}C. Zeta PALS from Brookhaven is used for the measurements of zeta potential discussed in previous section 3.1.16. Detailed measurement procedure has been discussed in section 4.7. Carbonate rocks are positively charged due to the presence of cations on the mineral surface. Different concentrations of VES solution are treated with rock powder and supernatant solutions are analyzed for zeta potential. Negative values of zeta potential are

obtained. The values of zeta potential decreased until 0.5% and then started to increase slightly with the increase in concentration of VES. This could be due to adsorption of VES on the rock. But once VES is adsorbed until 0.5% the values tend to decrease after that because maximum amount of VES has been adsorbed. Also, because VES solution is more viscous than VES-CA solutions, the adsorption is more in this case.

4.11.2 Effect of VES/CA Solutions

Zeta potential measurements between VES-CA solutions of different concentrations and powdered rock from Wafra Ratawi formation is presented in Figure 66. Solutions are prepared by keeping the VES concentration constant of 0.3% and changing the concentration of chelating agent from 0.1-1% with sea water of salinity 57,642 ppm and their zeta potential is determined. Solution preparation has been already discussed in section 4.1.4. All zeta potential measurements are performed at 25^{o}C. Zeta PALS from Brookhaven is used for the measurements of zeta potential discussed in previous section 3.1.16. Detailed measurement procedure has been discussed in section 4.7. Negative values of zeta potential are obtained. It can be observed that negative values are obtained using VES-CA solutions. Chelating agent of high pH value is used to reduce the adsorption. The negative values of zeta potential with VES-CA solutions treated with powdered rock decreased until 0.3% of chelating agent concentration and then increased with increasing the concentration of chelating agent used. VES-CA solutions are less viscous than VES solutions as results described in rheological characterization in previous section 5.9. It is seen that chelating agent is decreasing the zeta potential value until 0.3% and after that tends to increase with the increase in concentration of chelating agent. This may be because of chelating agent that it reduces the adsorption of VES on the rock surface.

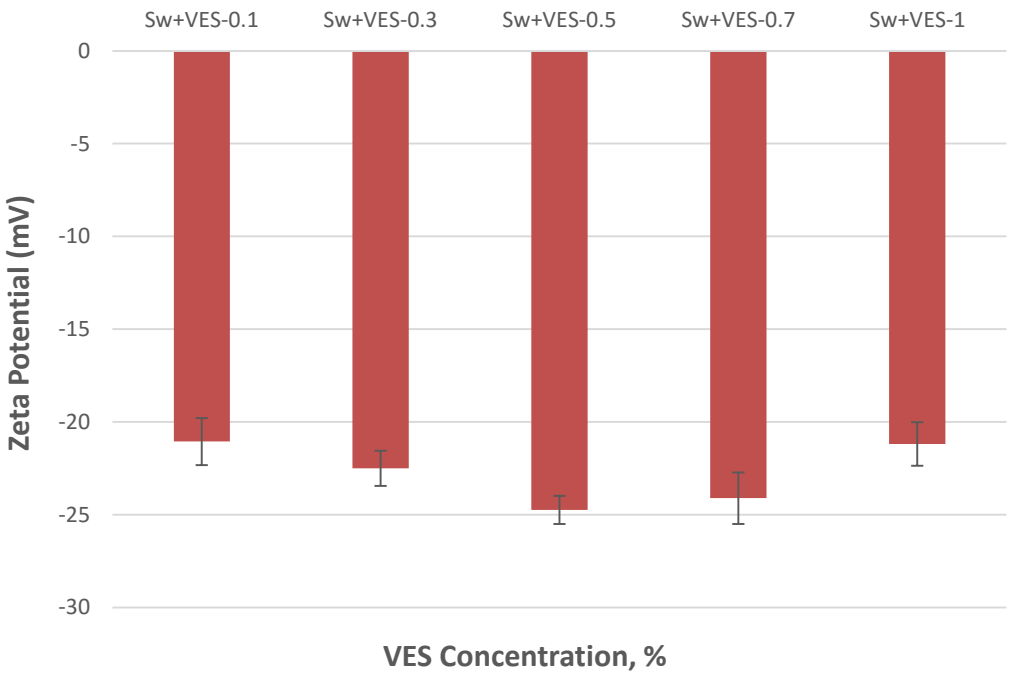

Figure 65: Zeta potential measurements of 0.3% VES treated with rock

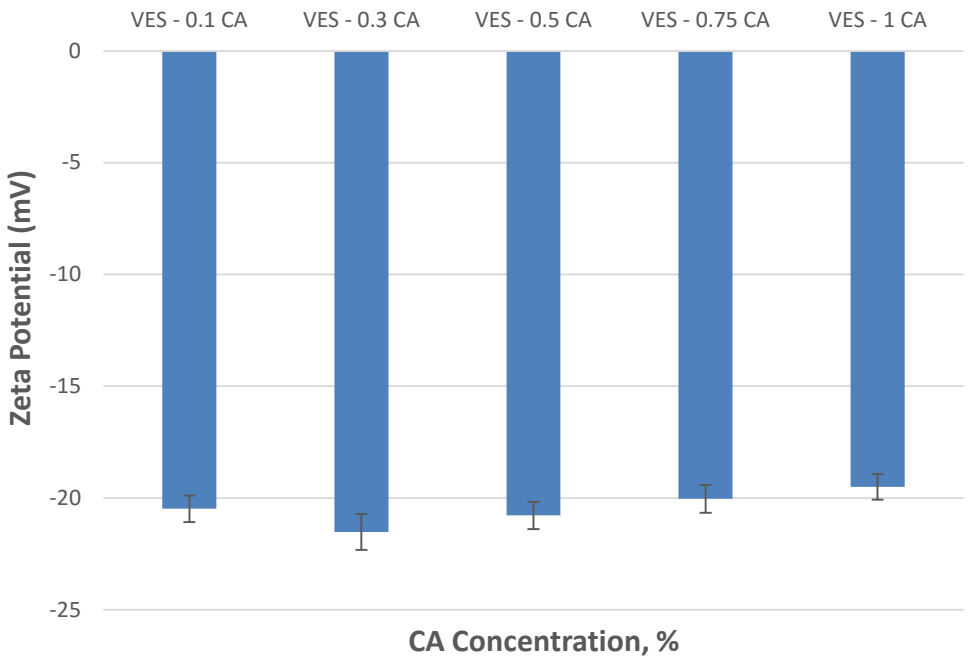

Figure 66: Zeta potential measurements of 0.3% VES and CA treated with rock

4.12 Core Flooding

Core flooding experiments are performed to analyze the potential of VES and VES-CA in recovering the oil from the reservoir. Core flooding studies are done on Wafra Ratawi formation samples at 90^{o}C. Core flooding starts with core preparation, aging the samples for 15 days, pore volume measurements, permeability measurements, initial water saturation, water flooding and then VES or VES-CA flooding. Equipment used for the experiments is discussed in 3.1.17. Detailed stepwise procedure for core flooding is discussed in previous section 4.8. Figure 67 shows the schematic of core flooding system. Results obtained with both experiments of core flooding are discussed in the next sections. In this phase of experiments, the optimum VES and VES/CA systems that pass the IFT, thermal stability, adsorption and as well as compatibility tests are subjected to performance evaluation in coreflooding.

4.12.1 Core flooding with VES

Core flooding with VES is discussed in this section. Core samples used for this experiment are 4A, 52 and 54. The porosity, permeability, length, diameter and total pore volume for each core sample is presented in Table 4. Optimum VES concentration is selected from all the tests performed and is used for this experiment. Optimum VES of concentration 0.3% is selected from IFT/viscosity ratio. Solution of 0.3% VES is prepared as discussed in section 4.1.3. Crude oil of 17^{o} API is used from Wafra Ratawi. Sea water of salinity 57,642 ppm is used for water flooding and its preparation is discussed in section 4.1.1. Permeability measurements, connate water saturation, water flooding and VES flooding results are discussed. Effluents collected from the core flooding are analysed for concentration analysis. Temperature condition used for the experiment is 90^{o}C.

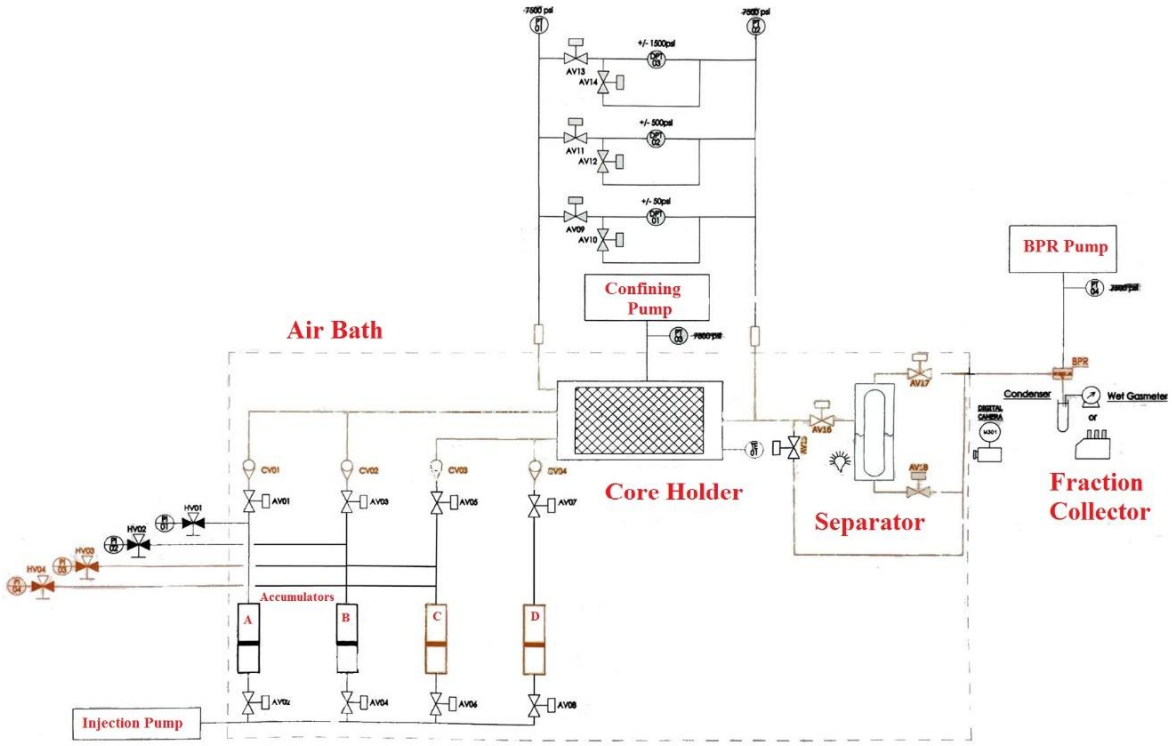

Figure 67: Schematic of core flooding system

Permeability Measurement

Darcy law is applied for the permeability measurements which states that velocity of homogeneous fluid in porous medium is directly proportional to the pressure gradient and inversely proportional to the viscosity.

$$v = \frac{q}{A} = \frac{k*dP}{\mu*L} \quad (10)$$

Where

$v =$ Velocity of fluid in $\frac{cm}{s}$

q = flow rate in $\frac{cm^3}{s}$

k is the absolute permeability in Darcy

d P is the differential pressure in atmosphere

μ is the viscosity of the injected fluid in cP

L is the length of the core in cm

A is cross sectional area in cm^2

$$\frac{q}{dP} = m = \frac{A*K}{\mu*L} \quad (11)$$

$\frac{q}{dP}$ is the slope (m) to be determined

The slope is determined by flowing the formation brine at different flow rates and measuring their corresponding dP's. Table 9 gives the data obtained for the determination of slope and the rate(q) and change in pressure (dP) are converted into appropriate units for use in the Darcy law. Figure 68 shows the plot of q vs dP and the slope is measured.

Table 9: Slope determination parameters for core flooding with VES

q, cc/min	q, cc/sec	dP, Psi	dP, atm
0.5	0.00833	3.4	0.23136
1	0.01667	6	0.40828
1.5	0.025	8.6	0.5852
2	0.03333	11.8	0.80294
2.5	0.04167	14.1	0.95945

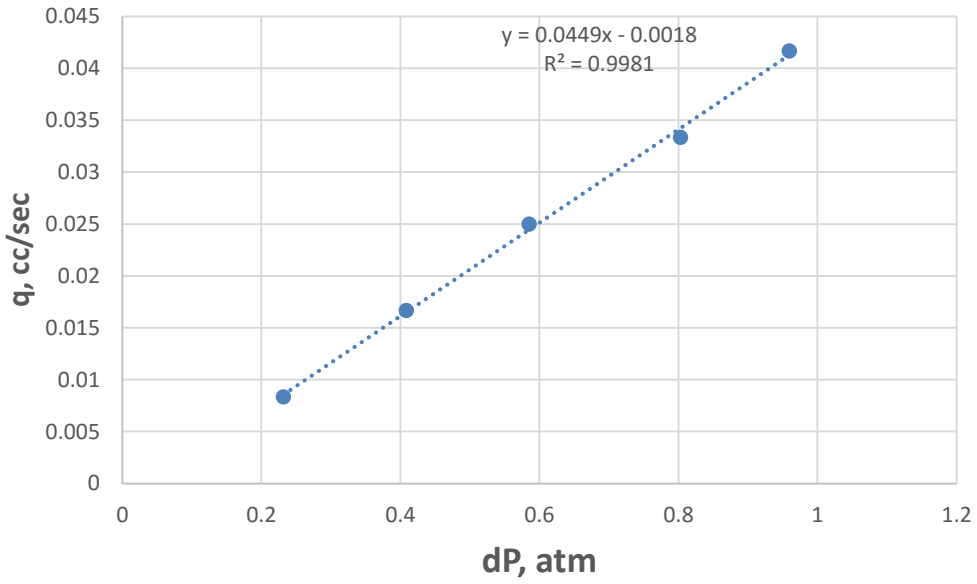

Figure 68: Determination of slope for permeability measurement

Slope obtained by plotting the flow rate (q) on y-axis and pressure drop (dP) on x-axis is 0.044 from Figure 68. Substituting the slope value in the darcy law and other parameters are known. Permeability can be find out as:

Diameter of core = 3.76 cm

Cross sectional area = $\frac{\pi}{4} * d^2$

Length of core = 13.501 cm

Viscosity of formation brine = 1cP

By substituting the values in darcy law equation (9)

$$q = \frac{kA}{\mu}\frac{dP}{L}$$

Rearranging,

$$\frac{q}{dP} = \ 0.044 = \frac{\frac{3.1416}{4} * d^2 * k}{\mu * L}$$

k = 53.5 milli darcy

The permeability obtained by flowing formation brine through the cores is 53.5 md for samples used for VES flooding.

Initial Water Saturation

For the calculation of remaining oil, it is necessary to find out the initial water saturation inside the cores. The cores are flooded with oil and the formation brine recovered is collected in a cylindrical flask. Calculations are done to measure initial water saturation as:

Total Pore Volume = 38.67 ml

Total water recovered = 28.47 ml

Water recovery factor = $28.47/38.67 * 100 \ =$ 73.62% or 0.7362

So,

Initial water saturation = $1 - 0.7362 = 0.263$ or 26.3%

This means that 26.3% of formation brine is residing in the smaller pores of the core samples and is immobile.

Water Flooding and VES flooding

Determination of permeability and initial water saturation leads us to the aging process. Oil is injected in the cores until no more formation brine is produced at the outlet. Then the cores saturated with oil are subjected to aging for 15 days. The temperature of the system is kept constant at 90^{o}C during the whole aging process. Once aging is complete, the sea water injection is done at the rate of 0.5ml/min. Sea water is injected for 4 PV's to ensure that all the oil that can be recovered from cores is taken out. Recovery obtained by injecting sea water is almost 35%. Cores used are highly permeable so most of the oil is recovered with the sea water.

VES solution of 0.3% was chosen to be optimum from the viscosity/IFT ratio. Though higher concentration gives more viscosity/IFT ratio but the 0.3% is selected based on the IFT results and economics. 0.3% VES is injected after sea water injection and the additional oil recovery is noted. 0.3% VES is injected for 2 PV's and the recovery factor is calculated. Recovery factor obtained with 0.3% VES is almost 41%. The additional recovery obtained with the 0.3% VES is 6%. Additional recovery obtained is due to the dual capability of VES to reduce the IFT and improve the mobility ratio. The pressure at the inlet and outlet of the core is constantly monitored and the change in pressure is noted. Oil rate and water rate are calculated. All the parameters like recovery factor, pressure drop, oil rate and water rate are plotted in one graph and is presented in Figure 69. It is

clear from the plot that oil recovery is increased by injecting 0.3% VES after the sea water. The pressure drop is decreasing until 6 PV's but then suddenly increases. Figure 70 shows the pressure drop profile against injected pore volume for VES injection only. It can be seen that pressure drop increase has occurred. This effect can be due to the shear thinning behavior of VES when it encounters the less permeable region. It enters the less permeable region and blocks some of the pores which can be efficient to block thief zones in the reservoir. Elasticity may also influence the increase in pressure drop. More oil can be displaced with the improved sweep efficiency. VES as a single fluid has the dual capability of reducing the IFT and improving the mobility or sweep efficiency. As the production of oil started the oil rate begins to drop and water rate goes increasing. This depends on the production of oil per pore volume.

Effluent Analysis

The effluents collected from the core flooding are subjected to concentration analysis using TOC for each pore volume. Figure 71 shows the trend of VES concentration with the pore volume injected. The trend is zero until 4 PV's because there was no injection of VES. From 4 PV's to 7 PV's VES injection started and the concentration started to increase. From 7 PV's onward sea water injection again started and the concentration of VES started to decrease.

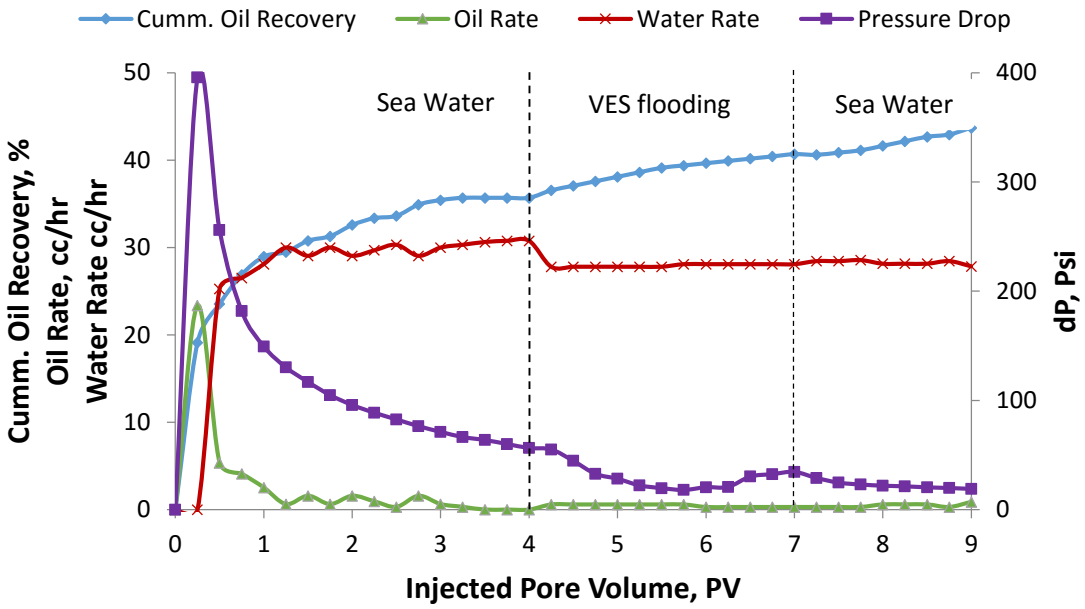

Figure 69: Core flooding with 0.3% VES

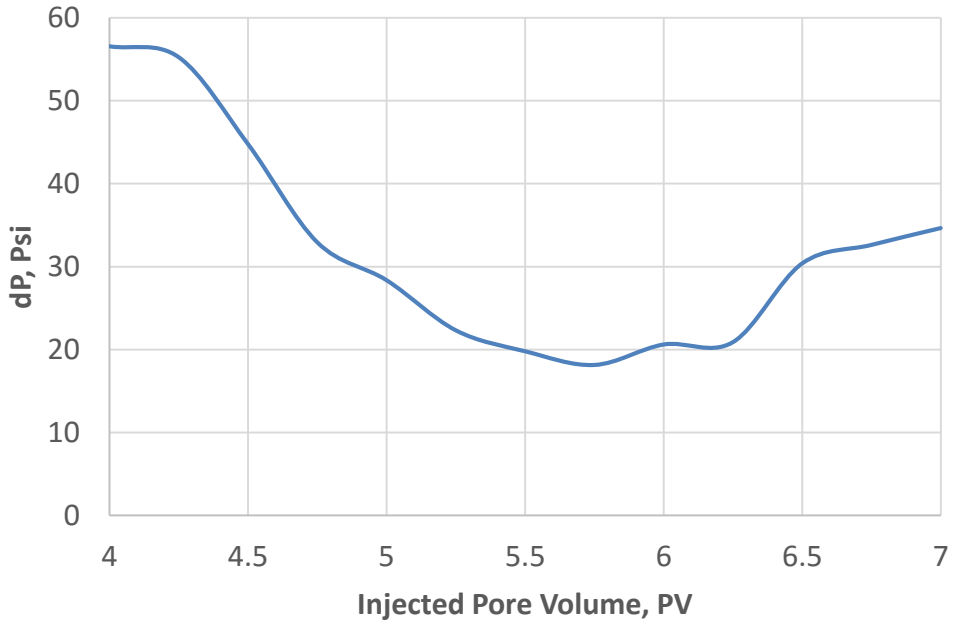

Figure 70: Pressure drop profile with 0.3% VES

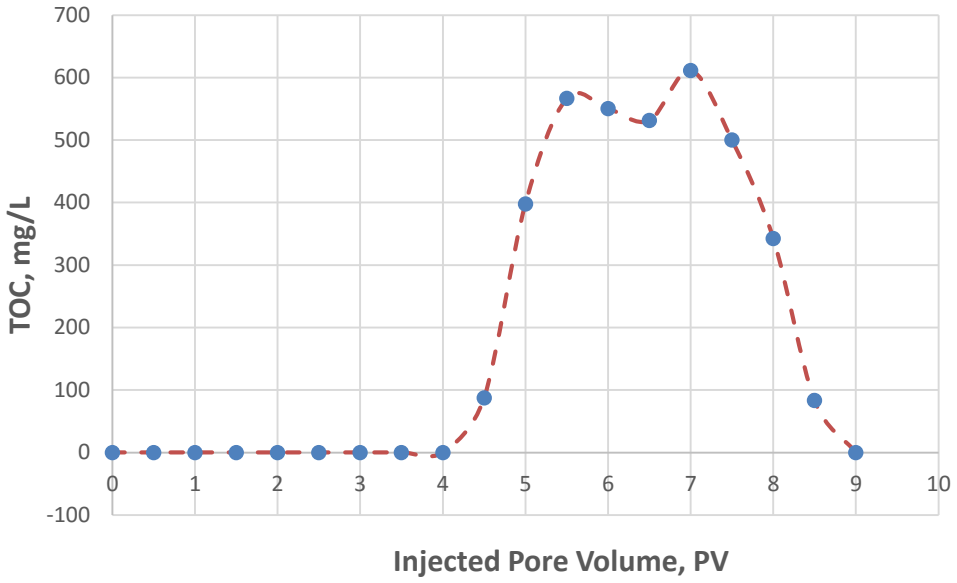

Figure 71: Effluent analysis of core flooding with 0.3% VES

4.12.2 Coreflooding with VES/CA

Core flooding with VES-CA is discussed in this section. Core samples used for this experiment are 3, 64 and 69. The porosity, permeability, length, diameter and total pore volume for each core sample is presented in Table 5. Optimum chelating agent concentration is selected from all the tests performed and is used for this experiment. Optimum VES of concentration 0.3% is selected from IFT/viscosity ratio. Solution of 0.3% VES 0.3% CA is prepared as discussed in section 4.1.4. Crude oil of 17^{o} API is used from Wafra Ratawi. Sea water of salinity 57,642 ppm is used for water flooding and its preparation is discussed in section 4.1.1. Permeability measurements, connate water saturation, water flooding and VES-CA flooding results are discussed. Temperature condition used for the experiment is 90^{o}C.

Permeability Measurement

Darcy law is applied for the permeability measurements same as used for VES flooding.

$$v = \frac{q}{A} = \frac{k*dP}{\mu*L} \quad (12)$$

Where

$v =$ Velocity of fluid in $\frac{cm}{s}$

q = flow rate in $\frac{cm^3}{s}$

k is the absolute permeability in Darcy

d P is the differential pressure in atmosphere

μ is the viscosity of the injected fluid in cP

L is the length of the core in cm

A is cross sectional area in cm^2

$$\frac{q}{dP} = m = \frac{A*K}{\mu*L} \quad (13)$$

$\frac{q}{dP}$ is the slope (m) to be determine

The slope is determined by flowing the formation brine at different flow rates and measuring their corresponding dP's. Table 10 gives the data obtained for the determination of slope and the rate(q) and change in pressure (dP) are converted into appropriate units for use in the Darcy law. Figure 72 shows the plot of q vs dP and the slope is measured. Slope obtained by plotting the flow rate (q) on y-axis and pressure drop (dP) on x-axis is 0.052 from Figure 72. Substituting the slope value in the darcy law and other parameters are known. Permeability can be find out as:

Diameter of core = 3.756 cm

Cross sectional area = $\frac{\pi}{4} * d^2$

Length of core = 12.726 cm

Viscosity of formation brine = 1cP

By substituting the values in darcy law equation (11)

$$q = \frac{kA}{\mu}\frac{dP}{L}$$

Rearranging,

$$\frac{q}{dP} = 0.052 = \frac{\frac{3.1416}{4} * d^2 * k}{\mu * L}$$

k = 59.7 milli darcy

The permeability obtained by flowing formation brine through the cores is 59.7 md for samples used for VES flooding.

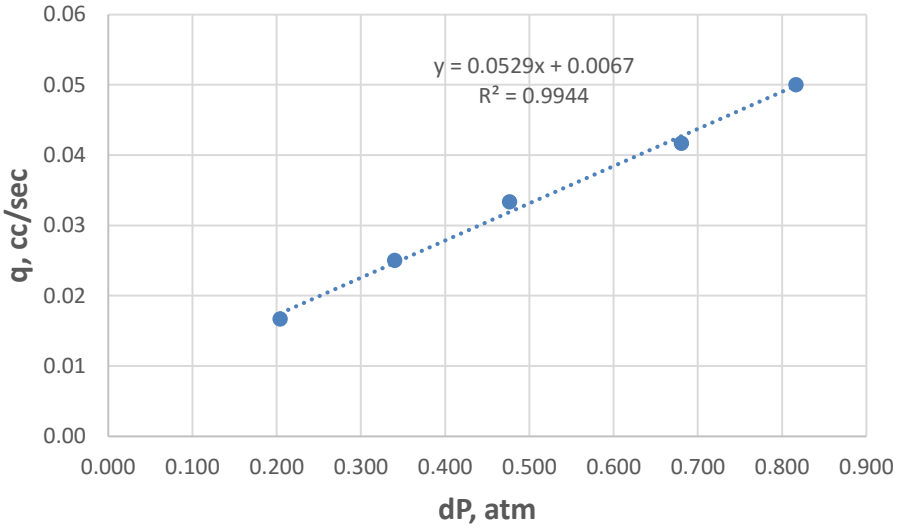

Figure 72: Determination of slope for permeability measurement

Table 10: Slope determination parameters for coreflooding with VES-CA

q, cc/min	q, cc/sec	dP, Psi	dP, atm
1	0.017	3	0.204
1.5	0.025	5	0.340
2	0.033	7	0.476
2.5	0.042	10	0.680
3	0.050	12	0.817

Initial Water Saturation

For the calculation of remaining oil, it is necessary to find out the initial water saturation inside the cores. The cores are flooded with oil and the formation brine recovered is collected in a cylindrical flask. Calculations are done to measure initial water saturation as:

Total Pore Volume = 38.31 ml

Total water recovered = 31.47 ml

Water recovery factor = $31.47/38.31 * 100 = 82.16\%$ or 0.8216

So,

Initial water saturation = $1 - 0.8216 = 0.1784$ or 17.84%

This means that 17.84% of formation brine is residing in the smaller pores of the core samples and is immobile.

Water and VES-CA Flooding

Determination of permeability and initial water saturation for second experiment leads us to the aging process. Oil is injected in the cores until no more formation brine is produced at the outlet. Then the cores saturated with oil are subjected to aging for 15 days. The temperature of the system is kept constant at 90^{o}C during the whole aging process. Once aging is complete, the sea water injection is done at the rate of 0.5 ml/min. Sea water is injected for 5 PV's to ensure that all the oil that can be recovered from cores is taken out. Recovery obtained by injecting sea water is almost 41.5%. Cores used are highly permeable so most of the oil is recovered with the sea water.

0.3% VES solution was chosen to be optimum from the viscosity/IFT ratio. Though higher concentration gives more viscosity/IFT ratio but the 0.3% is selected based on the IFT results and economics.0.3% CA is chosen based on the results from IFT discussed in

section 5.7.1. 0.3% VES 0.3% CA is injected after sea water injection and the additional oil recovery is noted. 0.3% VES 0.3%CA is injected for 4 PV's and the recovery factor is calculated. Recovery factor obtained with 0.3% VES 0.3% CA is almost 47.32%. The additional recovery obtained with the 0.3% VES 0.3%CA is almost 6%. Additional recovery obtained is due to the dual capability of VES to reduce the IFT and also improve the mobility ratio. From the results of IFT we know that CA has not contributed much to reduction in IFT when mixed with 0.3%VES. The pressure at the inlet and outlet of the core is constantly monitored and the change in pressure is noted. Oil rate and water rate are calculated. All the parameters like recovery factor, pressure drop, oil rate and water rate are plotted in one graph and is presented in Figure 73. It is clear from the plot that oil recovery is increased by injecting 0.3% VES 0.3% CA after the sea water. The pressure drop is decreasing till the end. Figure 74 shows the pressure drop profile against injected pore volume for VES-CA injection only. Pressure drop is decreasing with time and has not increased like VES injection. This effect can be due to the less viscous solution of VES-CA. VES is elastic in nature and the effect of elasticity is reduced by the addition of chelating agent as discussed in previous section of rheological characterization 5. 9.2. As the production of oil started the oil rate begins to drop and water rate goes increasing. This depends on the production of oil per pore volume.

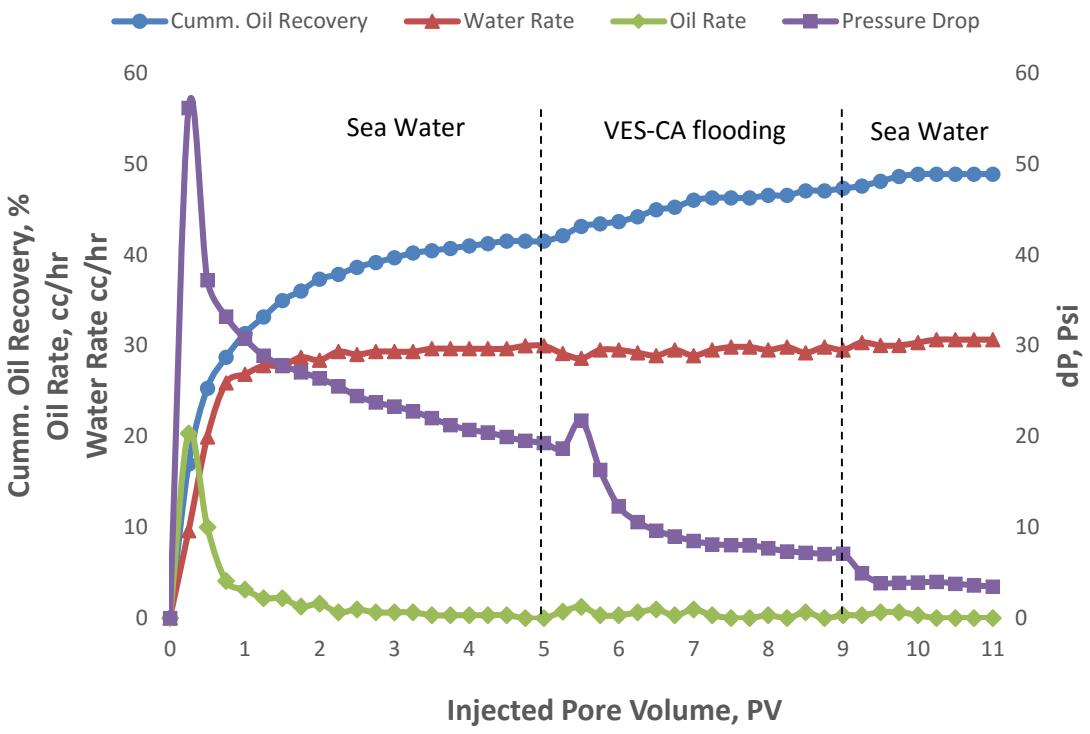

Figure 73: Core flooding with 0.3% VES 0.3% CA

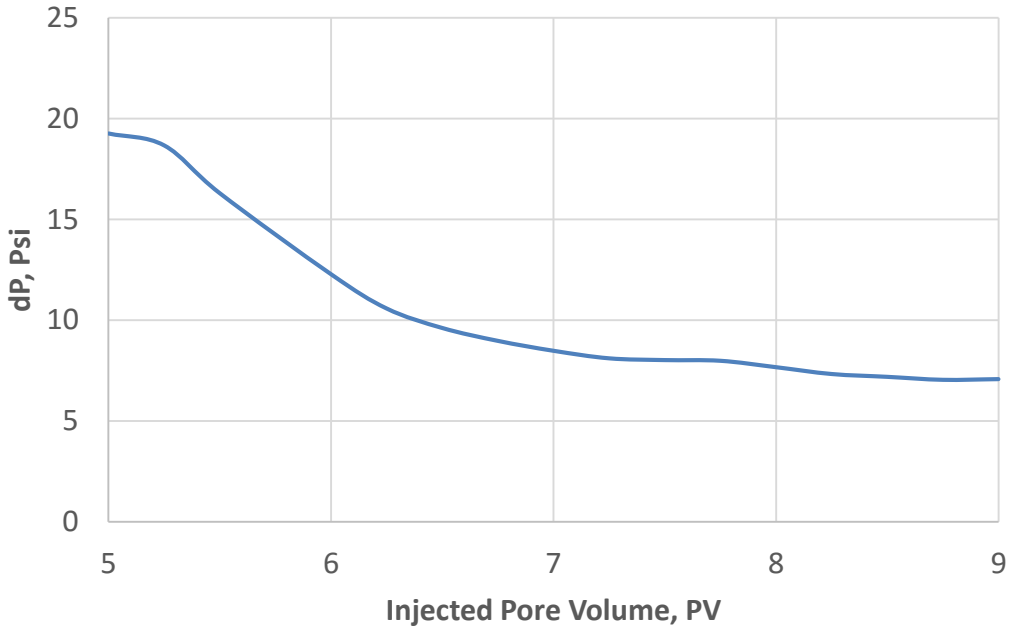

Figure 74: Pressure drop profile with 0.3% VES 0.3% CA

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

Based on the results obtained, following conclusions were made from the extensive study on the potential of viscoelastic surfactant:

1. Viscoelastic surfactant is used that can provide both the functions of reducing the interfacial tension and also improving the displacement/sweep efficiency of the reservoir.
2. Effect of concentration, temperature and time on the IFT reduction is evaluated. From all those parameters, optimum concentration of VES is selected.
3. The optimum concentration of VES selected is used with high pH chelating agent DTPA to notice the effect of chelation on IFT reduction. It is observed that addition of chelating agent to VES does not give much reduction in IFT than only VES.
4. Thermal stability of the VES systems is evaluated. Both the short term and long term thermal stability is determined. It is observed that VES has high thermal stability in short term aging.
5. Long term thermal stability is evaluated by aging the VES system at two high temperatures of 90^{o}C and 120^{o}C. Parameters like IFT reduction, viscosity measurements, FTIR and NMR are performed to study the desired objective. It is seen that IFT increases after aging the samples at high temperatures. At very high

temperatures the viscosity also drops. FTIR and NMR results are interpreted and show loss of some carbon elements from the chemical composition.

6. Static adsorption is measured by equilibrating the solid crushed Wafra Ratawi sample with VES systems. Adsorption experiments are performed at two different temperatures of 30^{o}C and 60^{o}C. It is observed that adsorption was more in the case of low temperature while at high temperature adsorption was less. The calculated adsorption was then matched with the Langmuir isotherm model and BET isotherm model. Both the models match very perfect with our experimental data.
7. Experiments related to zeta potential are performed to analyze the results of adsorption and correlate them. It is found that negative values are obtained for both VES and VES/CA systems that are tested. Negative values increase until some concentration and then decreases for both the systems.
8. Core flooding with VES and VES/CA systems are performed, and the results are evaluated. Total additional recovery of about 8% is obtained from VES and 7.4% from VES/CA systems which means chelating agent is not much adding to the additional oil recovery.

5.2 Recommendations

1. Laboratory experiments are conducted with VES systems. The applicability of these systems can be studied by performing molecular simulation and pore scale study for various conditions.
2. Chelating agents of different pH can be analyzed for the future studies to enhance the recovery potential.

3. Experiments related to Wafra Ratawi crude oil are performed. This may also be extended to other field crude oils.
4. Contact angle measurement experiments need to be conducted for VES systems with carbonate reservoirs.
5. After evaluating the VES systems for all the screening criteria of EOR, they may be pilot test on field.

APPENDICES

APPENDIX A: VISCOSITIES OF FLUIDS

VISCOSITY OF OIL

Table 11: Viscosity of Oil at different temperatures

Temperature (^oC)	Viscosity (cp)
30	452.05
50	94.99
70	41.44
90	12.11

VISCOSITY OF VES

Table 12: Viscosity of VES at different concentrations at 30^oC

Concentration (wt %)	Viscosity (cp)
0.1	4.637
0.3	23.690
0.5	31.986
0.75	48.465
1	93.800

APPENDIX B: DENSITIES OF FLUIDS

DENSITY OF OIL

Table 13: Densities of crude oil at different temperatures

Temperature (ºC)	Density (g/cc)
30	0.939
50	0.925
80	0.846

DENSITY OF VES

Table 14: Densities of VES solutions at different temperatures

Temperature (ºC)	Concentration (%)	Density (g/cc)
30	0.1	1.036
	0.3	1.0359
	0.5	1.0375
	0.75	1.0367
	1	1.0359
50	0.1	1.027
	0.3	1.0258
	0.5	1.0262
	0.75	1.0279
	1	1.0249
80	0.1	1.0052
	0.3	1.0006
	0.5	1.0028
	0.75	1.0048
	1	1.0004

DENSITY OF VES-CA

Table 15: Densities of VES-CA solutions at different temperatures

Temperature (ºC)	Concentration (%)	Density (g/cc)
30	0.1	1.0398
	0.3	1.0406
	0.5	1.0417
	0.75	1.0428
	1	1.0434
50	0.1	1.0306
	0.3	1.0307
	0.5	1.0327
	0.75	1.0341
	1	1.0347
80	0.1	0.9999
	0.3	1.0033
	0.5	1.0051
	0.75	1.0117
	1	1.0115

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